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PHASE EQUILIBRIUM IN THE SYSTEM: $Li_2O \cdot Al_2O_3$–SiO_2*

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ABSTRACT

Liquidus and solidus temperatures for almost all of the 21 preparations along the line $Li_2O \cdot Al_2O_3$–SiO_2, from 85 to 22 per cent silica, have been determined. Three component compounds in the system are β-spodumene ($Li_2O \cdot Al_2O_3 \cdot 4SiO_2$, high temperature form, melts congruently at 1423°C.) and β-eucryptite ($Li_2O \cdot Al_2O_3 \cdot 2SiO_2$, melts with dissociation at 1397°C.). No compounds having the compositions of petalite ($Li_2O \cdot Al_2O_3 \cdot 8SiO_2$) or "lithium orthoclase" ($Li_2O \cdot Al_2O_3 \cdot 6SiO_2$) are stable above the solidus. Petalite dissociates at 950°C. or less.

This system includes five or six fields: (1) the silica field, (2) the field of β-spodumene-silica solid solution, (3) the field of β-spodumene solid solution, (4) the field of β-eucryptite solid solution, (5) the γ-alumina field, and (6) the lithium aluminate field (?). Fields (1) and

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(2) appear to be binary; fields (3) and (4) are essentially binary at the liquidus but show ternary behavior 10° to 80° below the solidus, small amounts of mullite and/or α-alumina separating from the solid solution series; field (5) is ternary.

Attempts to synthesize α-spodumene (mineral) hydrothermally at pressures below 100 atmospheres and at temperatures of 400° to 550°C. failed. In every case β-spodumene crystallized from the spodumene glass.

INTRODUCTION

The alkali aluminosilicates are among the most important rock-forming minerals in nature. The phase equilibrium relationships in the potassium and sodium aluminosilicate systems have been partly determined. However, little is known about such relationships in the lithium aluminosilicate system.

The ternary system, $Li_2O–Al_2O_3–SiO_2$, contains three compounds that occur in nature: eucryptite ($Li_2O \cdot Al_2O_3 \cdot 2SiO_2$), spodumene ($Li_2O \cdot Al_2O_3 \cdot 4SiO_2$), and petalite ($Li_2O \cdot Al_2O_3 \cdot 8SiO_2$). Because these three compounds all have a molecular ratio of one to one between lithia and alumina, it seemed desirable to first investigate the composition line extending from silica to $Li_2O \cdot Al_2O_3$.

The lithium aluminosilicate minerals are not abundant in nature but they are important constituents of lithium pegmatites. A possible clue to the physical-chemical conditions under which these minerals are formed in the pegmatites is furnished by this investigation. The existence or absence of other compounds in the system, such as "lithium orthoclase" ($Li_2O \cdot Al_2O_3 \cdot 6SiO_2$) also may be of interest to the geologist and the mineralogist.

Furthermore, because lithia imparts many desirable properties to glasses and glazes, and because spodumene and petalite are sometimes used as a source of lithia, the investigation may be of interest to the ceramic and glass industries.

PREVIOUS INVESTIGATIONS

Investigations of the system $Li_2O \cdot Al_2O_3–SiO_2$ have been confined mainly to the synthesis of eucryptite, spodumene, and petalite, and to the determination of the melting and inversion temperatures of these compounds. Most of the investigations were made before 1914, all of them before 1921. Since then, our knowledge of silicate systems has increased manyfold and the techniques of thermal, microscopic, and x-ray analysis have been perfected and coordinated to an ever-increasing degree. It is to be expected, therefore, that much of the earlier data are inaccurate, especially the temperature determinations.

Possibly the earliest attempt to synthesize lithium aluminosilicates was reported by Hautefeuille[15] in 1880. He prepared compounds of

$LiO\cdot \mathrm{Al_2O_3\cdot 5SiO_2}$ (1:1:5),* (1:1:6), and (3:4:30) by fusion of the ingredients with lithium vanadinate or tungstate as a flux. In 1890, Hautefeuille and Perrey[16] reported the synthesis of the lithium equivalent of nepheline, now known as eucryptite (1:1:2).

Many other attempts to synthesize eucryptite, spodumene, and petalite have been made by Weyberg[31] (1905), Stein[27] (1907), Ginsberg[14] (1912), Endell and Rieke[10] (1912), Ballo and Dittler[2] (1912), and Jaeger and Simek[17] (1914). It was generally recognized by these men that the physical properties of the synthetic compounds differed from those of the mineral of corresponding composition.

Investigations on the inversion of the lithium aluminosilicate minerals were confined almost entirely to spodumene. Brun[6] (1902) and Tammann[28] (1903) noted that the density of spodumene decreased markedly when heated for a short time at a temperature of about 1000°.† By means of specific gravity—temperature and refractive index—temperature curves Endell and Rieke[10] showed that spodumene underwent a change at 950° but thought this to be the melting temperature. Ballo and Dittler,[2] Jaeger and Simek,[17] and Meissner[22] (1920) concluded that the inversion of α-spodumene (mineral) to the high temperature β-form was monotropic. Endell and Rieke also noted that petalite became isotropic-amorphous at 1050°.

Of the several determinations of the melting temperatures of the lithium aluminosilicate minerals (M) and synthetic products (S) (see Table 1), only the method of "quenching" used by Jaeger and Simek gave

TABLE 1. REPORTED MELTING TEMPERATURES OF PETALITE, SPODUMENE, AND EUCRYPTITE

Name	Date	Petalite	Spodumene	Eucryptite	Method
Cusack[8]	1897	—	(M) 1173°	—	Meldometer
Brun[6]	1902	(M) 1270°	—	—	—
Doelter[9]	1907	—	(M) 1080°	—	PtRh thermel, heating curve.
Ginsberg[14]	1912	—	—	(S) 1307°	Cooling curve
Endell,[10] Rieke	1912	(M) 1050° (1340°)	(M) 950° (1380°)	—	PtRh thermel, heating curve.
Ballo,[2] Dittler	1912	(S) 1200°	(S) 1275°	(S) 1330°	PtRh thermel, cooling curve.
Fletcher[12]	1913	—	(M) 1223°	—	Meldometer
Jaeger,[17] Simek	1914	—	(M) 1418–1428° (S) 1401–1420°	(S) 1388°	PtRh thermel, quench method.

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* Hautefeuille used the formula LiO for lithium oxide.

† All temperatures in this report are in degrees Centrigrade.

good results. The cooling curve method gave low results because of the marked undercooling of lithium aluminosilicate melts. Another source of error in the determination of the melting temperature of spodumene was the failure of several early workers to recognize that the swelling and powdering of spodumene when heated above 900° were inversion phenomena instead of melting.

For a more general review of the literature the reader is referred to Mellor's[23] treatise.

EXPERIMENTAL PROCEDURE

MATERIALS

The silica was obtained from colorless rock crystal quartz that contained only a few small inclusions of gas bubbles and magnetite. The crystals were crushed in a steel mortar, the powder treated with hot hydrochloric acid to remove traces of iron, and then inverted to cristobalite by heating in an electric furnace to a temperature of about 1400° for about twelve hours. The silica was then ground in an agate mortar, the powder treated with hot aqua regia to remove traces of platinum. The purified silica yielded a residue of 0.02 per cent when evaporated with hydrofluoric and sulfuric acids.

The alumina was obtained from the General Chemical Company. A spectrographic analysis of the alumina revealed the presence of sodium as the most abundant impurity. The material was purified by boiling three times in ammonium chloride solution followed by washing with hot water. The alumina was then fired. A quantitative spectrographic analysis of the purified material showed that most of the sodium had been removed and that not more than 0.05 per cent soda remained.

As a source of lithia, Baker's lithium carbonate was used. A quantitative spectrographic analysis indicated that the amount of soda present was not greater than 0.15 per cent ($Li_2O + Na_2O = 100\%$). The material was used without further purification.

THE $Li_2O \cdot Al_2O_3$–SiO_2 PREPARATIONS

The lithium aluminosilicate glasses were prepared by three methods: (1) by adding a constant amount of alumina and a variable amount of silica to previously prepared lithium silicate glass or crystalline material; (2) by mixing two lithium aluminosilicate glasses; and, (3) by adding a variable amount of silica to crystalline $Li_2O \cdot Al_2O_3$.

The advantage of the first method is that no further volatilization of lithia is detected when the alumina and silica are added to the lithium silicate. Also, this method permits the fixation of lithia at a much lower temperature than is possible in any other way. The second method allows additional intermediate glasses to be prepared quickly and easily. The third method is probably best for mixtures low in silica. Most of the preparations were made by the first two methods.

The lithium aluminosilicate glasses were made in a platinum crucible by melting the ingredients in an electric furnace at about 1500°. To ensure homogeneity of the glasses, the batches were crushed, mixed, and melted five successive times. The products appeared to be homogeneous when examined under a petrographic microscope.

As a check on the accuracy of the synthesis of the glasses, seven of them were analyzed chemically. One-half gram samples were fused with sodium carbonate, dissolved in hydrochloric acid, and dehydrated and filtered twice to separate the silica from the filtrate. Pure silica was determined by evaporating the impure silica with hydrofluoric and sulfuric acids. Alumina was determined by precipitation with 8-hydroxyquinoline.

The results of the chemical analyses (Table 2) show that all of the glasses contain silica and alumina within ± 0.2 per cent of the intended values. The probable limit of error of the analyses for both silica and alumina is ± 0.2 per cent.

TABLE 2. QUANTITATIVE CHEMICAL ANALYSES OF $Li_2O \cdot Al_2O_3$–SiO_2 GLASSES

No. of Prep.	Weight per cent SiO_2		Weight per cent Al_2O_3	
	Calc.	Anal.	Calc.	Anal.
3	78.5	78.4	16.7	16.8
6	64.6	64.6	27.4	27.5
8	56.0	56.0	34.0	34.2
9	53.0	53.0	36.4	n.d.
10	47.7	47.8	40.5	40.4
19	46.0	45.9	41.8	n.d.
20	44.0	44.1	43.3	n.d.

As a further check on the accuracy of the synthesis of the glasses, their refractive indices were determined (Table 3) and plotted as a curve (Fig. 1). The measurements were made on the water-quenched, unannealed glasses, using the oil immersion method and sodium (D) light. The temperature varied from 22° to 28°. After matching the refractive indices of glass and oil, the index of the oil was determined immediately by means of the Abbe refractometer.

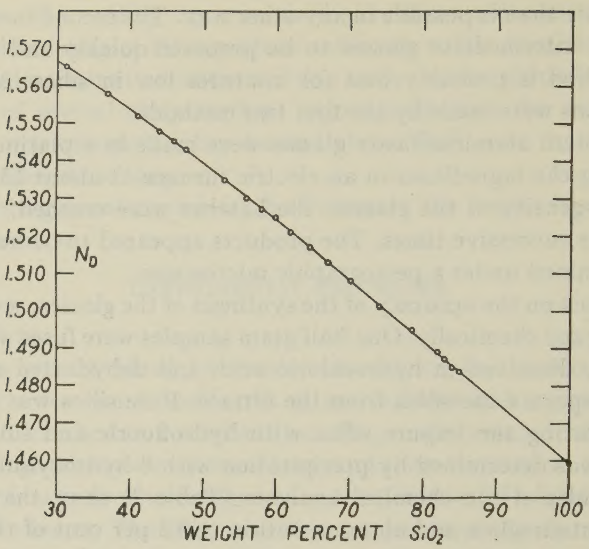

FIG. 1. Refractive index—composition curve of $Li_2O\cdot Al_2O_3$-SiO_2 glasses.

TABLE 3. REFRACTIVE INDICES OF $Li_2O\cdot Al_2O_3\cdot SiO_2$ GLASSES

No. of Prep.	Weight per cent SiO_2	Refr. Index
*	100	1.459
1	85.0	1.484
16	84.0	1.485
15	83.0	1.487
2	82.0	1.489
3	78.5	1.495
4	74.0	1.501
5	70.0	1.508
33	67.0	1.513
6	64.6	1.517
32	62.0	1.521
7	60.0	1.525
24	58.0	1.527
8	56.0	1.530
9	53.0	1.535
10	47.7	1.543
19	46.0	1.545
20	44.0	1.548
21	41.0	1.552
13	37.0	1.558
12	31.3	1.565

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* R. B. Sosman, The Properties of Silica, *Monograph Am. Chem. Soc.*, No. **37**, 592-4 (1927).

The limit of error in index is believed to be ±0.001; all the determined points lie within this range of the curve. From 100 per cent silica to about 55 per cent, the relationship is linear, within the limit of error. Below about 55 per cent the curve departs from the straight line in increasing amount. Because of the high melting point and the great rapidity of crystallization, it is not possible to extend the curve much below 31 per cent silica.

THE PHYSICAL EQUIPMENT AND EXPERIMENTAL CONDITIONS

A detailed description of the furnaces, the thermoregulator, and the thermocouple that were used in the investigation was given by Faust[11] who constructed the physical plant. The only noteworthy change in equipment was the substitution of a Leeds and Northrup type K potentiometer for the Wolff model used by Faust. The potentiometer-thermocouple system was not shielded.

Most of the temperature measurements were in the range from 1340° to 1430°. At these elevated temperatures it was difficult to keep the temperature of the "hot spot" constant. Most serious in its effect on temperature control was the fluctuation in the current output of the motor-generator. Unless compensated for manually, temperature fluctuations of 10° to 15° would occur several times a day. In spite of this difficulty, however, the temperature was kept constant to within five degrees during most runs and to within three degrees on most of the critical runs made to locate melting temperatures more accurately.

It was not possible to make accurate night runs due to the current fluctuations and also to volatilization of the platinum wire with which the furnace was wound. The latter caused a drop in temperature of three to ten degrees overnight.

All temperature measurements were made with a Pt: 90Pt 10Rh thermocouple that was calibrated at the following fixed points:

Gold	1062.6°C.
Diopside ($CaMgSi_2O_6$)	1391.5°C.

Because most of the temperatures measured were within ±40° of the diopside melting temperature, this calibration point was used almost exclusively to correct the potentiometer readings. A calibration was made after almost every determination of a liquidus or solidus temperature. Electromotive force readings were converted into temperatures by means of standard tables.[1] The diopside was kindly furnished by the Geophysical Laboratory.

TABLE 4. LIQUIDUS AND SOLIDUS TEMPERATURES OF $Li_2O \cdot Al_2O_3$–SiO_2 PREPARATIONS

Prep. No.	Composition, weight per cent			Liquidus temp. °C.	Time, hours	Primary phase	Solidus temp. °C.	Time, hours	Phases
	Li_2O	Al_2O_3	SiO_2						
1	3.4	11.6	85.0	1382 ± 5	8–12	Tridymite	1356 ± 3	3–5	Tridymite + β-spodumene-silica solid solution
16	3.6	12.4	84.0	1367 ± 3	6–10	β-spodumene-silica s.s.	n.d.		S.S. + tridymite
15	3.9	13.1	83.0	1371 ± 3	3–6	Ditto	n.d.		Ditto
2	4.1	13.9	82.0	1380 ± 3	2–6	Ditto	n.d.		Ditto
3	4.9	16.6	78.5	1397 ± 3	6–10	Ditto	1355 ± 5	10–12	Ditto
4	5.9	20.1	74.0	1413 ± 3	8–12	Ditto	1365 ± 5	10–12	β-spodumene-silica s.s.
5	6.8	23.2	70.0	1420 ± 4	12–15	Ditto	n.d.		Ditto
33	7.5	25.5	67.0	n.d.		Ditto	1404 ± 5	8–11	Ditto
6	8.0	27.4	64.6	1423 ± 3	6–20	β-spodumene	None		
32	8.6	29.4	62.0	n.d.		β-spodumene s.s.	1407 ± 5	11–12	β-spodumene s.s.
7	9.1	30.9	60.0	1418 ± 4	11–12	Ditto	1408 ± 5	9–13	β-spodumene s.s. + β-eucryptite s.s.
24	9.5	32.5	58.0	1412 ± 4	6–11	Ditto	1402 ± 4	7–11	β-eucryptite s.s.
8	10.0	34.0	56.0	1406 ± 4	7–11	β-eucryptite s.s.	n.d.		Ditto
9	10.6	36.4	53.0	1403 ± 4	10–12	Ditto	1399 ± 4	9–11	Ditto
10	11.8	40.5	47.7	1397 ± 4	9–11	β-eucryptite	None		
19	12.2	41.8	46.0	1421 ± 3	3–4	γ-alumina	1390 ± 4	8–12	γ-alumina + β-eucryptite-like s.s. (dissociates)
20	12.7	43.3	44.0	1450 ± 5	3–4	Ditto	1387 ± 5	7–12	Ditto
21	13.4	45.6	41.0	1490 ± 5	2–6	Ditto	1376 ± 5	7–13	Ditto
13	14.3	48.7	37.0	n.d.		Ditto	1361 ± 5	7–14	Ditto
12	15.7	53.1	31.3	n.d.		Ditto	1340 ± 5	6–12	γ-alumina + lithium aluminate-like s.s. (?)
22	17.7	60.6	21.7	n.d.		Ditto	1371 ± 5	9–12	Ditto
				TERNARY COMPOSITIONS OFF THE LINE					
17	5.9	10.1	84.0	1290 ± 5	4–13	Tridymite	1140 ± 20	12–24	Tridymite + an unidentified phase
18	3.0	13.0	84.0	n.d.		Mullite	n.d.		
28	6.3	28.9	64.8	1425 ± 5	2–12	Mullite	1385 ± 5	2–15	Mullite + β-spodumene-silica s.s.
29	10.0	24.4	65.6	1415 ± 6	2–12	β-spodumene-like phase	1400 ± 10	6–12	Peculiar dissociation of homogeneous phase, no mullite
31	20.4	39.0	40.6	1343 ± 20	24	γ-alumina	n.d.		

Note: s.s. = solid solution.

The high viscosity of the lithium aluminosilicate melts made it necessary to employ the "quench method" for determining melting temperatures. This method was originally described by Shepherd, Rankin, and Wright[26] in 1909 and has since been mentioned many times in the reports of the members of the Geophysical Laboratory of the Carnegie Institution. As is usually the case in investigations of this kind, these experiments were carried out in an oxidizing atmosphere and under a pressure of one atmosphere.

EXPERIMENTAL RESULTS

The data presented in Table 4 and Fig. 2 represent a summary of the many quenching experiments made during the investigation of this problem. A brief outline of the principal facts follows.

From 100 per cent silica to 64.6 per cent (β-spodumene) the system appears to be binary and is divided into fields of silica and β-spodumene-silica solid solution by a eutectic point at 84.5 per cent and 1356°. The solid solution extends up to about 76 per cent silica beyond which tridymite crystallizes as the secondary phase. Petalite (78.5 per cent) or "lithium orthoclase" (73.2 per cent) are not stable at the liquidus. Only β-spodumene has a clearly defined congruent melting temperature at about 1423°.

From 64.6 to 47.7 per cent silica (β-eucryptite) the system behaves essentially like a binary system above the solidus and is divided into fields of β-spodumene solid solution and β-eucryptite solid solution by a peritectic point at about 57.3 per cent. Above the solidus in both of the fields the solid solutions show an increasing amount of dissociation into an unknown fibrous product as the silica decreases. At temperatures ranging from 10° to 80° below the solidus these fields show ternary behavior with small amounts of mullite forming in the β-spodumene solid solutions and somewhat larger amounts of mullite and/or α-alumina forming in the β-eucryptite solid solution. The compound β-eucryptite is unstable and dissociates into γ-alumina and a β-eucryptite-like substance just below 1397°, the liquidus temperature.

From 47.7 to less than 22 per cent silica the system is ternary and passes through the γ-alumina field. A secondary phase of β-eucryptite-like solid solution (unstable) extends from 47.7 to 31.3 per cent and at a lower silica content than 31.3 per cent the secondary phase is a lithium aluminate (?) solid solution.

With this brief summary of the system to serve as a guide, some of the fields will be described in greater detail.

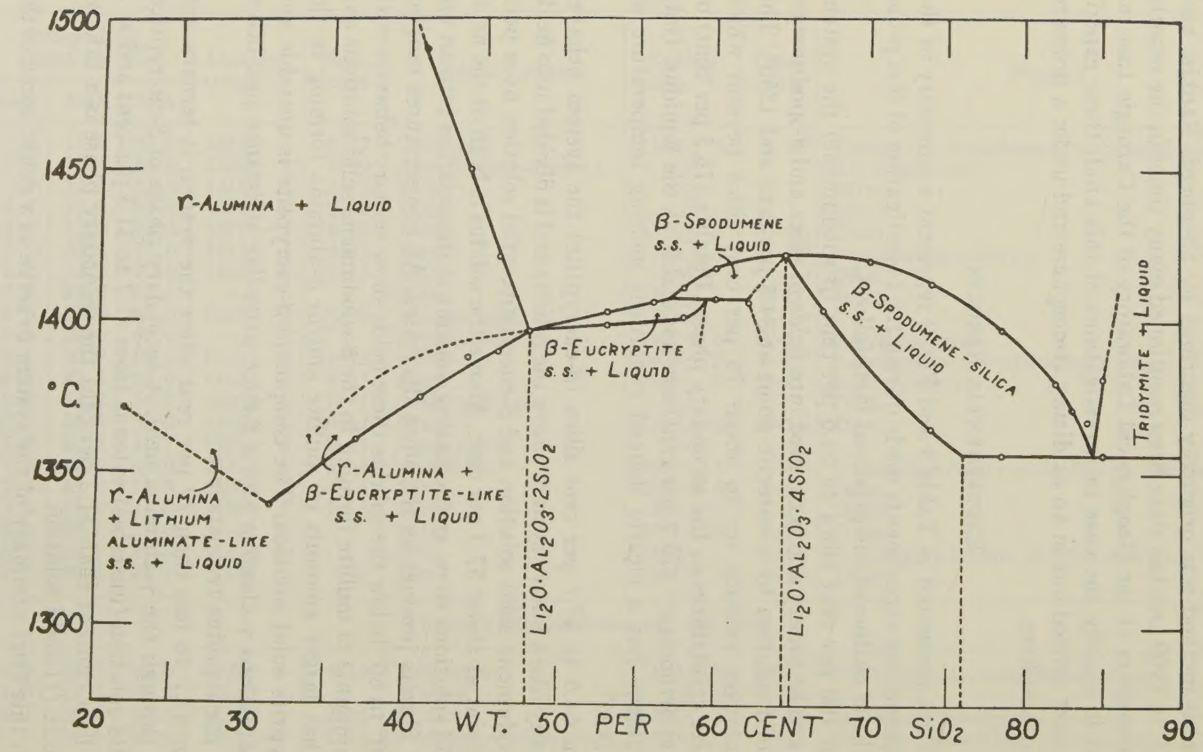

FIG. 2. Liquidus and solidus curves of $Li_2O \cdot Al_2O_3$–SiO_2 preparations.

THE SILICA FIELD

The liquidus curve was not determined for this field because the high temperature causes rapid burning out of the furnace. An additional difficulty is the very great viscosity of the melts in the silica field. The reluctance of crystalline phases to go into solution makes it difficult to prepare homogeneous glasses.

The liquidus curve may be located approximately by constructing a curve through the points 100 per cent, 1713° and 85 per cent, 1382°. The latter point lies just within the silica field with tridymite the primary phase. The shape of the liquidus is probably similar to that determined by Kracek[20] for the silica field in the system, Li_2O–SiO_2.

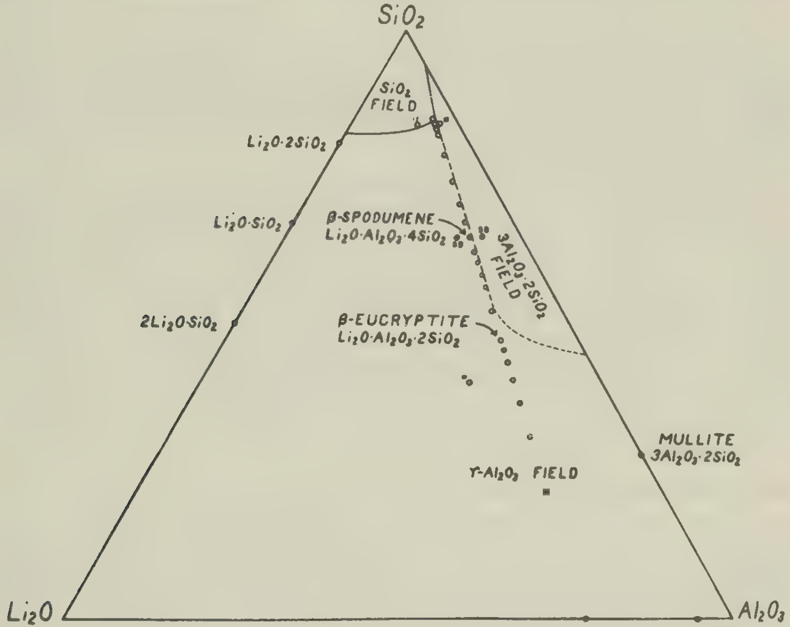

FIG. 3. Fields in the system Li_2O–Al_2O_3–SiO_2.

The approximate boundary of the silica field in the ternary system Li_2O–Al_2O_3–SiO_2 may now be established from the data of Kracek, Bowen and Greig,[5] and the writer. This and the location of all compositions investigated by the writer are plotted in Fig. 3.

THE FIELD OF β-SPODUMENE-SILICA SOLID SOLUTION

The determination of the liquidus curve for this field presented no great difficulty. Although the viscosity of the melts increases directly with the silica content, the time necessary to obtain equilibrium decreases markedly. It is doubtful if twelve hours is sufficient time to obtain equilibrium in melts with a silica content less than 70 per cent.

The solidus curve is located only approximately but the general character of the curve is probably correct. The existence of solid solution was established by optical and *x*-ray powder examination of the crystalline products. A fairly regular variation in the spacing of the lines on the *x*-ray photographs and a small but regular variation of the refractive indices constitute the evidence for solid solution.

No compound or solid solution with the composition of petalite exists at temperatures above about 950°. Synthetic material of the composition of petalite was held at temperatures ranging from 1356° down to about 1140°, and all contained 10 to 15 per cent of an interstitial glass-like phase which probably is silica in some form.

Samples of the mineral petalite when heated at temperatures of about 950° and 1050° for 12 and 7 hours, respectively, dissociated to a crystalline product having the same optical properties as the synthetic material of the same composition and contained 10 to 15 per cent of the same interstitial glassy phase. *X*-ray powder photographs of both of these products were quite similar. The liquidus temperature of an unaltered, pure-looking petalite from Greenwood, Maine (U.M. no. 4170), was determined to be 1399°. This value compares favorably with the 1397° obtained for the artificial product.

THE SOLID SOLUTION FIELDS OF β-SPODUMENE–β-EUCRYPTITE

General considerations: The determinations of liquidus and solidus temperatures in these fields were especially difficult because all compositions tend to superheat and the refractive indices of the glasses are very close to those of the crystalline products. According to Morey,[24] "overheating is a common occurrence," especially in complex silicate melts. That superheating takes place in this system is not surprising because this phenomenon has long been recognized in the corresponding potassium and sodium aluminosilicate systems.

In order to approach equilibrium conditions the samples must be held for long periods of time at a constant temperature. For reasons mentioned previously, it was not possible to make constant temperature runs of much longer duration than about twelve hours. Runs of one hour duration gave liquidus temperatures about five degrees higher than the values indicated in the phase diagram. It does not appear likely that periods of heating for longer than twelve hours would lower the liquidus temperatures appreciably.

The crystalline products have a marked tendency to recrystallize and to become coarse-grained when held near their melting temperatures, both above and below. When the grains begin to melt, the product is a granular aggregate of crystalline material with discrete grains of glass and not the normal interstitial arrangement of glass. Measurements of the refractive indices of the glasses indicate that the crystal aggregates melt to liquids having compositions within one per cent silica of the composition of the sample, the compositions usually lying on the high silica side of the point rather than on the low silica side as expected. All this is indicative of superheating.

Glasses in the β-spodumene–β-eucryptite fields devitrify readily when heated between 1000° and 1100° for fifteen minutes. *X*-ray powder photographs of the devitrified materials reveal a fairly regular shift of the lines of high-angle reflection indicating complete solid solution between the two end components. Beta-eucryptite solid solutions when heated near the solidus temperature give *x*-ray patterns which are closely similar, if not entirely identical, with those obtained from the devitrified glasses, but preparations in the β-spodumene field when subjected to the same treatment show patterns similar to the devitrified glasses but contain more lines of high-angle reflection. This probably indicates minor structural changes in the β-spodumene solid solution, possibly due to the exsolution of a second crystalline phase.

In addition to the thermal evidence for a peritectic point at 57.3 per cent silica and 1408°, there is ample optical evidence of such a reaction. The β-spodumene-like material is uniaxial positive while the β-eucryptite solid solution is uniaxial negative; also, there is a small but easily determined difference in their refractive indices. An examination of samples of preparation no. 24 reveals all stages in the transition of the crystalline product from the β-spodumene phase to the β-eucryptite phase, with decrease in temperature. Attention is called to the material no. 24-I (Table 5) which originally formed β-eucryptite solid solution when heated at about 1355° but inverted back to a β-spodumene-like phase when heated between 1400° and 1405°. This indicates that the inversion temperature may be somewhat lower than the 1408° indicated in the phase diagram.

The field of β-spodumene solid solution: As a check on the melting temperature of artificial β-spodumene, that of kunzite from Pala, California, was determined to be 1423° while that of spodumene from the Black Hills, South Dakota, was 1419°. The artificial material fuses at 1423°. These values fall within the 1418° to 1428° range given by Jaeger and Simek[17] for natural spodumenes.

The evidence for at least a limited solid solution in the β-spodumene field is revealed by: (1) a slight increase in the refractive indices of the crystalline products from 64.6 to 60 per cent silica; (2) x-ray powder photographs which show a small but fairly regular shift in the lines of high-angle reflection; (3) a solidus temperature for preparation no. 32 which is the same, or slightly less, than is shown by preparation no. 7; and, (4) the presence of a β-eucryptite-like phase as rims around the β-spodumene in preparation no. 7, when it is heated below the solidus for several hours. The writer tentatively interprets the β-spodumene field as consisting of a limited solid solution, extending between 64.6 and 62 per cent silica.

When preparations in this field are heated for about three to twelve hours or more, varying amounts of a fine-grained fibrous product exsolves from the solid solution. The resulting intergrowth may be likened to a film and fine string perthite, commonly observed in potash feldspar. The dissociation takes place above the solidus as well as below it; both substances, however, appear to melt at the same time, probably due to the superheating effect. The amount of this material and the rate at which it exsolves increase with decreasing silica, beginning with a trace in β-spodumene and increasing to a maximum at about 57 per cent silica. It develops first as short fibers perpendicular to the grain borders and spreads inward. The marked ability of the β-spodumene solid solution to recrystallize appears to cause expulsion of a part of this material from the grains and the development of interstitial stringers around the grains. Because of the very fine-grained nature of this exsolution product and the resulting interference of the host material, its optical properties are extremely difficult to determine. The coarser stringers are weakly birefringent and probably have positive elongation. The refractive index is noticeably greater than that of the host. Nothing is known about the composition of the exsolution product and therefore the direction of change in composition of the β-spodumene solid solution can not be predicted. Investigations off the $Li_2O \cdot Al_2O_3 \cdot SiO_2$ line may reveal the true nature of this dissociation.

Before leaving this subject several points concerning the peritectic reaction between β-spodumene and β-eucryptite solid solutions may be worth recording. The β-spodumene solid solution of preparation no. 24 dissociates rather rapidly above the inversion temperature and eventually completely, producing the typical intergrowth with the exsolution product. Below the inversion temperature the two phases react slowly to give a β-eucryptite solid solution which contains only a trace of the exsolution product.

In preparation no. 7 the phase that develops with long heating below the solidus as wide rims around the β-spodumene solid solution is optically positive, like β-spodumene, but it has refractive indices which are close to those for β-eucryptite. This material contains much of the exsolution product, probably giving aggregate indices, while the β-spodumene cores are comparatively free of the exsolution product. The supposition is that the material composing the rims will invert to β-eucryptite solid solution if given sufficient time.

The field of β-eucryptite solid solution: The case for solid solution in the β-eucryptite field is amply supported by optical and *x*-ray evidence. The refractive indices of the solid solution increase slightly with decreasing silica and the *x*-ray photographs show a regular shift in the lines of high-angle reflection.

This field consists essentially of one phase although a fine-grained fibrous material tends to exsolve with long heating, beginning along the borders of the grains and working inward. In appearance and behavior this exsolution product seems to be identical with the fibrous material described in the β-spodumene field.

Beta-eucryptite itself is a very unstable compound which dissociates with short periods of heating just below the melting temperature to a β-eucryptite-like phase that contains γ-alumina plus the above-mentioned fibrous material. The β-eucryptite-like substance has lower refractive indices than the true β-eucryptite compound, $\omega=1.528$, $\epsilon=1.521$, as compared to $\omega=1.531$, $\epsilon=1.523$.

It was not feasible to determine the melting temperature of natural eucryptite because it seems to occur always as a very fine-grained intergrowth with albite. The material that Jaeger and Simek[17] used was undoubtedly such a mixture. Dr. Foshag of the U. S. National Museum kindly furnished the writer with a sample of the eucryptite-albite material from Branchville, Connecticut (U.S.N.M., no. 81106), that was described by Brush and Dana.[7] The material melted to a glass having a refractive index of 1.506, the same value obtained by Jaeger and Simek. Artificial eucryptite glass has a refractive index of 1.543. According to Penfield's chemical analysis the intergrowth is composed of eucryptite and albite in a molecular ratio of one to one. If this ratio is changed into weight per cent; if 1.543 and 1.489 are used as the refractive indices of eucryptite and albite glasses, respectively; and, if perfect additivity is assumed; the refractive index of the glass obtained from such a mixture should be 1.506.

Ternary behavior of the β-spodumene-β-eucryptite fields: Several weeks before the experimental work was discontinued it was discovered that preparation no. 24 develops a small amount of a mullite-like phase when held at a temperature of 1355° for 28 hours. In the remaining time the writer attempted to discover how many other preparations exhibit a similar type of dissociation. The results of the few runs made are given in Table 5.

Table 5. Experiments on the Dissociation of β-Spodumene–β-Eucryptite Solid Solutions

Prep. no.	Temp. °C.	Time, hours	Results
3-P	1337–1350	37	No mullite.
5-C	1337–1350	37	1–2% mullite needles in β-spodumene-like phase.
33-C	1376–1392	70	Homogeneous solid solution.
6-C	1400–1405	9	Used 6-B. Mullite needles redissolved completely to form homogeneous β-spodumene.
6-A	1376–1392	70	Trace of mullite needles in β-spodumene.
6-B	1326–1340	30	1–3% mullite needles and wormy interstitial material in β-spodumene.
7-F	1376–1392	70	Typical exsolution product in β-eucryptite-like rims around the β-spodumene.
7-G	1326–1340	30	3–5% mullite needles in β-spodumene-like phase.
24-I	1400–1405	9	Used 24-G. Mullite needles redissolved completely leaving β-spodumene solid solution plus the fibrous exsolution product.
24-H	1384–1392	13	β-eucryptite solid solution, very little exsolution product. No mullite.
24-G	1348–1362	28	5–8% mullite needles, trace of α-alumina, in β-eucryptite-like phase.
8-A	1326–1340	30	3–5% mullite needles plus α-alumina in β-eucryptite-like phase.
9-C	1376–1392	70	5–10% α-alumina, trace of γ-alumina, no mullite, in β-eucryptite-like phase. Small amount of fibrous exsolution product.
9-D	1326–1340	30	3–5% α-alumina, trace of γ-alumina, no mullite, no fibrous exsolution product.
10-A	1376–1392	70	3–5% γ-alumina, trace of α-alumina, in β-eucryptite-like phase.
10-B	1337–1350	37	10–15% γ-alumina, trace of α-alumina, in β-eucryptite-like phase.

Several conclusions may reasonably be drawn from these experiments.

1. The region of dissociation to mullite extends from 70 per cent or greater to 56 per cent or less silica.
2. The β-eucryptite solid solutions dissociate to form an increasing amount of α-alumina and a decreasing amount of mullite as the β-eucryptite compound is approached.

3. The β-eucryptite compound dissociates mostly to γ-alumina with only a trace of α-alumina and no mullite.
4. Within certain limits, the amount of mullite or alumina increases with decreasing silica content, with decreasing temperature, and with increasing time.
5. The temperature of dissociation appears to be progressively higher with decreasing silica.
6. Very little or no fibrous exsolution product such as that which forms near the melting temperature is found associated with the mullite. Small amounts of it occur in some of the β-eucryptite samples that contain α-alumina and it seems to be more abundant in samples of 10 which contain γ-alumina.
7. The facts that good crystals of mullite in preparations nos. 6-C and 24-I completely redissolve when heated between 1400° and 1405° and that the fibrous exsolution product is present, lead one to doubt that the fibrous exsolution product is mullite in the incipient stage of formation. However, final judgment on this matter should await further experimental work in the ternary system.

The optical properties of the crystals thought to be mullite and α-alumina so far as they can be determined agree with the usual values for these substances. These data are presented in the section on Optical Data.

Conclusions: In the foregoing description of the β-spodumene–β-eucryptite fields of solid solution, the writer has attempted to show that the behavior of this part of the system above the solidus is essentially that characteristic of a binary system. The exsolution of a fine-grained fibrous product with long periods of heating, above as well as below the solidus temperatures, is strongly indicative of the metastability of the solid solutions. The development of small amounts of mullite or α-alumina at temperatures ranging from 10° to 80° below the solidus apparently indicates ternary behavior of the system at these temperatures.

Complete understanding of the unusual behavior of this part of the system must await further investigations in the ternary system. However, a clue was obtained from preparation no. 28 which is located on the alumina side of the line near the spodumene composition. This preparation lies in the mullite field and has liquidus and solidus temperatures of 1425° and 1385°. Mullite crystallizes out to the extent of 10 or 15 per cent before a lithium aluminosilicate, which probably has a composition close to 70 per cent silica, begins to crystallize at a temperature of about 1390°. This one observation suggests that the mullite field lies close to the $Li_2O \cdot Al_2O_3$–SiO_2 line, probably on the alumina side of the line but possibly extending slightly over the line to the lithia side (see Fig. 3).

This interpretation is supported by the marked similarity of the systems $MgO-Al_2O_3-SiO_2$[25] and $Li_2O-Al_2O_3-SiO_2$, due probably in part to the close similarity in the atomic radii of magnesium and lithium.

THE γ-ALUMINA FIELD

In the fields of β-spodumene and β-eucryptite solid solutions the tendency for a part of the alumina to break away from the lithium aluminosilicate solid solution is clearly recognizable below the solidus and is probably due to a gradual weakening of the chemical bonds that hold alumina in the structure. At a silica content of about 47.7 per cent the break is complete and γ-alumina becomes the primary phase in a field of ternary behavior. The γ-alumina field extends at least as far as 22 per cent. The writer has not investigated preparations of lower silica content because of the high melting temperatures. The liquidus and solidus curve do not reveal the changes in phase composition that take place in this field because the compositions of the phases lie off the $Li_2O \cdot Al_2O_3-SiO_2$ line.

In 1932 during an investigation of the $Li_2O-Al_2O_3-SiO_2$ system, Barlett[3] described what she thought to be a new cubic modification of alumina, called zeta-alumina. Subsequently, other investigators, such as Beljankin,[4] Verwey,[30] and Kordes,[19] expressed the opinion based on a comparison of refractive index, density, and *x*-ray measurements that zeta-alumina and γ-alumina are identical. The writer is not aware that any opinions to the contrary have been published. As the term γ-alumina was apparently first used by Ulrich[29] in 1925 for the cubic modification of alumina, it clearly has priority over the term "zeta-alumina."

The identification of γ-alumina was made more difficult when Kordes in 1935 claimed that he had synthesized a compound with a formula of $LiAl_5O_8$ which has physical properties that are nearly identical with those of γ-alumina. Both compounds have the spinel type of structure and give almost identical *x*-ray powder photographs.

In order to check on the identity of the γ-alumina produced in the study of this system, the writer had a quantitative spectrographic analysis made of the material. To separate the tiny crystals from the lithium aluminosilicate matrix, the material was decomposed with hydrofluoric acid and the lithium and aluminum salts dissolved in hydrochloric acid. After repeating this treatment, the γ-alumina crystals were separated from the acid solution by repeated decantations. The crystals appeared to be free from contamination when viewed under the microscope. The spectrographic analysis gave values of 2.2, 2.4, and 2.8 per cent lithia, which is about one-half of the 5.5 per cent contained in the lithium spinel.

The lithia content may have been due to (1) occluded lithium salt, (2) a mixture of lithium spinel and γ-alumina, or (3) solid solution between the two compounds. In view of the structural similarity of the two compounds, it is reasonable to expect partial if not complete solid solution between them. However, until the existence of the lithium spinel is verified, it is probably best to assume that this system contains only γ-alumina.

Barlett[3] noted that "crystals of the material (γ-alumina) remain unaltered when subjected to a temperature of 1600° for several hours. Fusing it, however, results in an inversion, apparently over a considerable period, to the alpha form. The presence of silica accelerates this change and causes it to occur at lower temperatures." The writer also observed a few small crystals of α-alumina associated with the γ-alumina in some of the samples that were heated at about 1400° for the longer periods of time. Many writers have indicated temperatures ranging from about 900° to 1200° for the γ- to α-alumina inversion. In most cases these results were obtained on γ-alumina prepared by dehydrating various hydrates of alumina. Both Verwey[30] and Kordes[19] state that the presence of a small amount of lithia stabilizes the lattice of γ-alumina. It appears likely that the γ-alumina in this system is metastable at temperatures above the solidus although the matter is not yet proved.

The marked similarity between this part of the system and the corresponding part of the MgO–Al_2O_3–SiO_2 system is worth noting. A large field of the structurally similar $MgO \cdot Al_2O_3$ spinel occurs in the latter.

It is readily seen in Fig. 2 that the temperature range through which γ-alumina crystallizes as the sole phase, increases rapidly between 47.7 and 31.3 per cent. The approximate boundary curve between γ-alumina and the secondary phase is shown in part by dashes. The secondary phase, from 47.7 through 37 per cent, shows a type of metastability similar to that observed in the β-eucryptite field. Under certain time-temperature conditions one homogeneous phase results; under different conditions there is extensive dissociation of this homogeneous phase into two phases. Lower temperature and longer periods of heating seem to be the conditions that favor the dissociation.

X-ray study of preparations nos. 19, 20, 21, and 13 reveals close similarity in structure between the homogeneous secondary phase and β-eucryptite; in fact there must be a β-eucryptite-like solid solution although neither *x*-ray nor refractive index measurements show unmistakable evidence of it. The uncertainty in estimating the amount of γ-alumina in the samples is too great to venture more than a guess on the compositions of the secondary solid solution phases. It appears likely, however, that they vary between β-eucryptite and some such possible compounds as 3:1:3 or 2:1:2. The dissociation of the secondary phase may take place into the end members of the solid solution series.

X-ray photographs of preparations nos. 12, 22, and $Li_2O \cdot Al_2O_3$ all show similar patterns with a progressive shift in some of the lines of high-angle reflection. The refractive indices of the three materials rise progressively and uniformly toward lithium aluminate and the birefringence is nearly identical in all. This is suggestive of a lithium aluminate-lithium aluminosilicate solid solution.

Inversion Temperatures

The lowest temperatures of α- to β-inversion on record are summarized as follows:

eucryptite,	never observed.
spodumene,	720° Meissner[22]
petalite,	950° (dissociates), this report.

Although the principal workers [2,10,17,22] concluded that the inversions of α- to β-spodumene and α- to β-eucryptite are monotropic, their experimental data are insufficient to prove it. However, all attempts to synthesize the natural compounds have failed even though the materials were mixed with tungstate and vanadinate fluxes and were fused at temperatures as low as about 600°. The marked decrease in density of spodumene when it inverts, from about 3.2 to 2.4, would seem to favor the monotropic inversion hypothesis for that mineral.

It is interesting to note that one method for the beneficiation of spodumene makes use of the α- to β-inversion.[13] In this process the spodumene-bearing rock is heated at 1050° to 1080° for about one hour to bring about the inversion. The β-spodumene powder is then easily separated from the quartz and feldspar gangue by a selective grinding process followed by a particle-size separation.

A similar treatment of petalite does not cause the mineral to powder because the change of volume which accompanies the dissociation is very small.

Hydrothermal Experiments

The hydrothermal synthesis of spodumene and petalite has never been attempted so far as the writer knows. The probable hydrothermal origin of these minerals made it highly desirable to attempt hydrothermal syntheses under different temperature and pressure conditions.

It may be stated at the outset that the results of these experiments thus far have been negative. No products resembling the natural minerals were formed. The data relating to the experiments are given in Table 6.

TABLE 6. DATA ON ATTEMPTED HYDROTHERMAL SYNTHESES OF SPODUMENE AND PETALITE

Exp. No.	1.	2.	3.
Temperature °C.	390°–430° aver. = 410°	ca. 550° (?)	410°–470° aver. = 440°
Pressure, (calc.)	11–15 atmos. aver. = 13 atmos.	ca. 20 atmos. (?)	60–90 atmos.
Time	14 days	ca. 5 hours, glass softened, bomb exploded	7 days or more, bomb exploded sometime during 14 day run.
Results	*Spodumene glass,* about ½ crystallized to fine-grained aggregate of β-spodumene. *Petalite glass,* no change.	*Spodumene glass,* entirely crystallized to β-spodumene. *α-spodumene,* no change. *Petalite glass,* no change. *α-petalite,* no change.	*Spodumene glass,* entirely crystallized to β-spodumene. *α-spodumene,* no change. *Petalite glass,* mostly glass, contains unidentified crystallites. *α-petalite,* no change.

The materials were wrapped in individual platinum foil envelopes and placed in the bombs with a known amount of distilled water. From the effective volume of the bomb (actual volume minus volume of samples) and the weight of water added, the reciprocal vapor density was calculated. With this figure and the temperature of the furnace during the run, the pressure was obtained from the steam tables of Keenan and Keyes.[18]

The bombs were heated to the desired temperature by placing them in an electric furnace, the "crystallizing furnace" described by Faust.[11] The temperature was measured before or after a run by means of a mercury in glass thermometer. The temperature range shown in Table 6 was caused by fluctuations in the voltage of the direct current source.

Pyrex glass tubing was used for the bombs but was serviceable only for relatively short runs at low pressures. The water vapor caused the crystallization of a thin layer of the glass on the inside of the tubes. Transverse and longitudinal cracks also formed on the inside and in time the weakened tube would explode.

Although the results of these experiments are negative, they indicate that spodumene and petalite probably do not form under low pressure hydrothermal conditions. It is always possible, however, that the time factor is of prime importance. If we recall the difference in density of α- and β-spodumene, it seems reasonable to expect that high pressure (500 to 1000 atmospheres) is a necessary condition for the formation of natural spodumene. The same can not be said for petalite because its density is about 2.5, not much greater than that of the high temperature dissociation product.

OPTICAL DATA

Tridymite: Crystals of tridymite are very small and not well developed. The refractive index is slightly less than 1.480, birefringence very weak.

β-spodumene-silica solid solution: Crystals of this solid solution series take the form of tetragonal bipyramids, well developed when formed in sufficient liquid, but becoming more granular as the amount of liquid decreases. The grain size ranges from a very fine-grained eutectic intergrowth of solid solution and tridymite, or siliceous glass, to grain diameters of 0.1 to 0.2 millimeter for β-spodumene. The solid solution material is uniaxial positive, ω=1.516 to 1.518, ε=1.517 to 1.523. The birefringence increases regularly from about 0.001 for the end member at 76 per cent silica up to about 0.005 for β-spodumene (see Fig. 4).

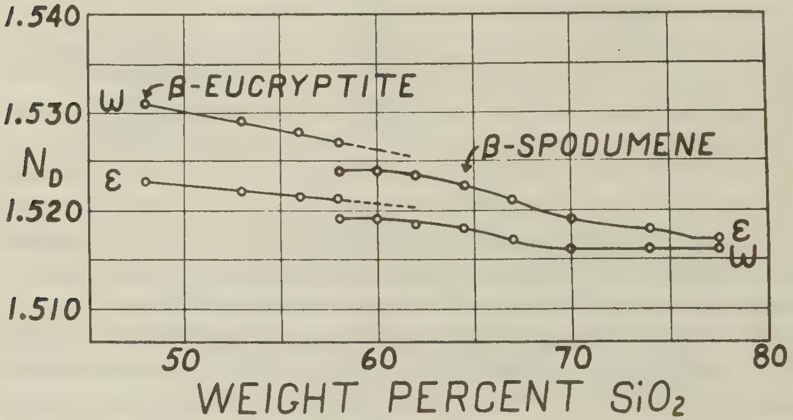

FIG. 4. Refractive index—composition curves of β-spodumene—β-eucryptite solid solutions.

β-spodumene solid solution: Crystalline material in this field forms irregular grains; no tetragonal crystals were ever seen. The material is uniaxial positive, probably tetragonal because of the close similarity in *x*-ray patterns of this material and that of the high silica solid solution field, $\omega = 1.518$ to 1.519, $\epsilon = 1.523$ to 1.524. The refractive indices increase very slightly with decreasing silica content. Jaeger and Simek[17] reported β-spodumene to be biaxial with a small 2V. However, such figures are obtained only on grains that show wavy extinction, as many of them do, which in some cases at least is due to overlapping crystals with different optical orientations.

β-eucryptite solid solution: This material takes the form of granular aggregates much like the β-spodumene. The material is uniaxial negative, probably tetragonal, $\omega = 1.527$ to 1.531, $\epsilon = 1.521$ to 1.523. The refractive indices increase slightly with decreasing silica content. A comparison of Figs. 1 and 4 reveals the interesting fact that the refractive indices of the glasses become greater than the mean index of the crystalline material for silica compositions below about 58 per cent. This indicates that the density of such glasses must be greater than that of the corresponding crystalline phases. Jaeger and Simek noted a three per cent increase in volume when eucryptite glass was devitrified. It is of interest to note that cordierite $2MgO \cdot 2Al_2O_3 \cdot 5SiO_2$ is quite similar optically to β-spodumene and β-eucryptite and also melts to a glass which has a refractive index greater than that of the crystalline material.

β-eucryptite-like solid solution: This material includes the homogeneous secondary phase in preparations nos. 19, 20, 21, and 13. All tend to crystallize as coarse-grained aggregates. The different materials seem to have identical optical properties. They are uniaxial negative, $\omega = 1.528$, $\epsilon = 1.521$.

Lithium aluminate-like solid solution (?): This material includes the secondary phase in preparations nos. 12 and 22 as well as lithium aluminate. All are uniaxial negative. The refractive indices are:

12.	22.	$Li_2O \cdot Al_2O_3$
$\omega = 1.586$	1.605	1.624
$\epsilon = 1.570$	1.589	1.606

A small amount of a third phase appears in preparation no. 22. It has refractive indices of about $\alpha = 1.576$, $\gamma = 1.583$, uniaxial negative (?).

γ-alumina: Crystals of γ-alumina are usually less than 0.01 millimeter in diameter. They are isotropic with octahedral habit, granular when poorly developed, refractive index of 1.733.

α-alumina: Crystals of α-alumina are usually about the same size as those of γ-alumina but can be readily distinguished from the latter by their hexagonal habit, forming thin hexagonal plates. These crystals are uniaxial negative and have a refractive index greater than 1.74. The relief and birefringence appear to be identical with known α-alumina placed in the same liquid.

Mullite: Crystals of mullite are developed the best in preparation no. 28 which lies in the mullite field. They occur as rectangular, needle-shaped crystals and have lengths up to about 0.05 millimeter. They have weak birefringence, parallel extinction, positive elongation, and a refractive index close to 1.65. The crystals which form in the β-spodumene–β-eucryptite fields are usually smaller but otherwise they have optical properties that agree with those above. The small size of the needles prevents satisfactory refractive index measurements. However, the needles in all stages of development and size appear like the mullite needles of corresponding development and size in preparation no. 28.

CONCLUSIONS

The system, $Li_2O \cdot Al_2O_3–SiO_2$, as far as it has been investigated, may be divided into five fields: (1) the silica field, (2) the field of β-spodumene-silica solid solution, (3) the field of β-spodumene solid solution, (4) the field of β-eucryptite solid solution, and (5) the γ-alumina field.

The compounds that exist in this system are silica (SiO_2, M.T. 1713°), β-spodumene ($Li_2O \cdot Al_2O_3 \cdot 4SiO_2$, M.T. 1423°), β-eucryptite ($Li_2O \cdot Al_2O_3 \cdot 2SiO_2$, M.T. 1397°), and lithium aluminate ($Li_2O \cdot Al_2O_3$, M.T. above 1600°). No compounds having the composition of petalite (1:1:8) or "lithium orthoclase" (1:1:6) are stable above the solidus. Petalite dissociates at 950° or less.

From 100 per cent silica to 64.6 per cent (β-spodumene) the system behaves like a binary system. A eutectic point exists between the fields of silica and β-spodumene-silica solid solution at 84.5 per cent and a temperature of 1356°.

The solid solution fields of β-spodumene and β-eucryptite extend from 64.6 to 47.7 per cent (β-eucryptite) and are separated by a peritectic point at 57.3 per cent and a temperature of 1408°, or slightly less. The relations in these two fields are essentially binary near the melting temperatures although a small amount of a very fine-grained fibrous material exsolves both above and below the solidus. At temperatures varying from 10° to 80° below the solidus, this portion of the system exhibits ternary behavior with the solid solutions partly dissociating to form small amounts of mullite or α-alumina. It is suggested that the unusual behavior of this part of the system may be due to the mullite field closely approaching or possibly crossing the $Li_2O \cdot Al_2O_3–SiO_2$ line as it does in the remarkably similar $MgO–Al_2O_3–SiO_2$ system.

With less than 47.7 per cent silica the system is ternary with γ-alumina the primary phase. The liquidus curve rises steeply to well over 1500° with a ten per cent decrease in silica. The γ-alumina appears to invert slowly with long heating near 1400° to α-alumina, thereby suggesting the metastability of the γ-form.

The attempts to synthesize α-spodumene hydrothermally at pressures below 100 atmospheres and at temperature of 400° to 550° all failed. In every case the high temperature β-form crystallized from the spodumene glass. Either higher pressures or longer time seem to be needed to form the mineral.

Although it is evident that this investigation is far from completion, the war makes it necessary to cease work on this problem. Most of the essential features of the system have been determined and it therefore seems advisable to publish the data as they now stand. The writer hopes that this work will provide a basis for further investigations in the ternary system Li_2O–Al_2O_3–SiO_2.

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THE CHEMICAL RELATIONSHIP OF CRYPTOMELANE (PSILOMELANE), HOLLANDITE, AND CORONADITE

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Abstract

The minerals cryptomelane, hollandite, and coronadite are isostructural and form isomorphous mixtures. The unit cell of the group contains 16 O ions. Its formula is:

$$\mathrm{Mn}^4{}_{8-(x/2+y/4+z/2)}\ (\mathrm{Mn}^2,\ \mathrm{R}^2)_x\ (\mathrm{K},\ \mathrm{Na})_y\ (\mathrm{Ba},\ \mathrm{Pb})_z\ 16\ \mathrm{O}\cdot(\mathrm{H_2O})_{2-(y+z)}$$

K, Ba, and Pb occupy identical positions. The ratio of $x:y:z$ is dependent on the state of oxidation of Mn which in turn depends on the conditions under which the mineral forms. H_2O occupies positions which could be filled by K, Ba, or Pb, provided electrostatic balance is maintained. The mineral called originally romanechite by Lacroix has been found to consist of minute crystals of cryptomelane.

Introduction

Few groups of minerals have caused more confusion for mineralogists and chemists than the manganese oxides. The reasons are either that they resemble one another and give tests which are not sufficiently distinctive for individual species or one is apparently working with a mixture of oxides. Psilomelane heads the list in this respect. Ramsdell (1) in 1932 had shown that "psilomelane" occurs in at least two different structures, one of which is high in Ba, the other contains little or no Ba. Lately he (2) has worked on the unit cell of the Ba-free variety to which Richmond and Fleischer (3) have given the name cryptomelane. The writer was investigating the same minerals when the work of Richmond and Fleischer was published. He was going to propose the name romanechite for this new species for reasons given below.

X-ray Investigation

Vaux (4) investigated Ba-psilomelane in 1937 by x-rays and proposed a unit cell and chemical formula. He restricted his work to a few specimens, particularly the material from Schneeberg, Saxony. Unfortunately he did not publish the x-ray spectra and the writer was unable to follow his work until he obtained Schneeberg specimens through the kindness of Dr. Samuel G. Gordon of Philadelphia (see Table 1).

TABLE 1. COMPARISONS OF POWDER SPECTRA
Unfiltered Fe Radiation.
Camera radius 57.3 mm.

Hollandite[1]		Cryptomelane[2]		Artificial Compound[3]		Psilomelane[4]	
d	*I*	*d*	*I*	*d*	*I*	*d*	*I*
6.83	2	6.81	2	6.8	3	3.880	1
4.81	2	4.87	2	4.88	2	3.462	2
3.442	1	3.469	0.5	3.452	0.5	3.320	1
3.077	5	3.084	5	3.077	4	3.239	1
2.467	0.5	2.455	1			2.877	2
2.389	3	2.393	2	2.389	5	2.418	2
2.192	2	2.196	1			2.361	1
2.137	2 *d*	2.148	1	2.150	1 *b*	2.255	1
1.939	0.5	1.929	0.5			2.191	3
1.907	0.5					2.150	1
1.820	2 *d*	1.827	2	1.817	1 *b*	2.021	0.5
1.622	1	1.637	1 *b*	1.610	1 *b*	1.820	2
1.535	3	1.538	3	1.532	2	1.709	0.5
1.432	1	1.428	1	1.428	1	1.635	1
1.353	1	1.353	2 *b*			1.559	2
1.345	1			1.341	1 *b*	1.497	0.5
1.300	0.5	1.294	1	1.295	0.5	1.422	2
						1.399	2
						1.296	0.5

b=wide line; *d*=double line.

[1] #8975 U.S. Nat. Museum. Chindwara Dist., India. Contains also some braunite, the lines of which have been omitted.

[2] Romanèche, Saône et Loire, France, #8137 Museum, Univ. of Minnesota.

[3] Reagent from Mallinckrodt. Was amorphous before heating for 24 hours at 500° C.

[4] Schneeberg, Saxony, #11050, Acad. Natural Sci., Philadelphia, Pa.

Vaux (4, p. 523) states that the psilomelane from Romanèche, Saône et Loire, France, gives the same *x*-ray spectra as the Schneeberg specimen. The same statement is made by Frondel (5, p. 55) in a very recent paper. Since there is no reason for doubting these statements, two varieties of "romanechite," as it used to be called, must occur at Romanèche, one of them a Ba-psilomelane and the other cryptomelane. There is a specimen at the University of Minnesota which A. Lacroix sent to N. H. Winchell in 1910, labelled romanechite from Romanèche. Since Lacroix (6, p. 6) himself described the mineral and as this description agrees with the specimen, there can be no doubt but that the material is from Romanèche. It is a beautiful specimen with a botryoidal surface covered completely with needles which are not longer than three-fourths of a millimeter. They are striated, but their terminal faces are too small for identification. The material under the botryoidal surface is also megascopically crystalline, but needles and massive material are intergrown and matted. Needles as well as the massive material give very good *x*-ray powder spectra of cryptomelane, as shown in Table 1. The streak of the mineral is almost black. The associated minerals are purple fluorite and white barite.

About six analyses of psilomelane from Romanèche are found in the literature (7 and 8). It is now impossible to correlate them with either one or the other of the two species. So far it has not been possible to obtain an analysis of the specimen described. It contains about 9 per cent BaO and 1 to 2 per cent H_2O. Most of this is not lost below 300°C.

As was already stated by Richmond and Fleischer (3), cryptomelane is a common mineral, more common than Ba-psilomelane. It may contain considerable amounts of Ba as just described, but Ba-psilomelane always contains this element in essential amounts. The *x*-ray patterns of the cryptomelanes may be quite sharp or they may consist of broad lines, the outer edges of which are difficult to measure. The difference in the quality of the spectra is not any greater than in kaolinites or goethites. Cryptomelane is stable to temperatures near 520°–540°C. The *x*-ray pattern changes to cubic Mn_2O_3 (bixbyite) above this temperature and to Mn_3O_4 (hausmanuite) at a much higher temperature. There is reason to believe that slight differences in composition of cryptomelane have considerable influence on this point of inversion.

Manganese dioxides, or compounds close to MnO_2 in composition, can be obtained as chemical reagents or precipitated in the laboratory. In either case there is no way of predicting whether the material will be essentially amorphous, or pyrolusite, or cryptomelane.

(a) A 20-year-old reagent of Mallinckrodt labeled "MnO_2, Binoxide Pure" is amorphous. When heated to 400°C. for 24 hours it did not crystallize, but above this temperature, and even as high as 525°C., it gave a relatively good pattern of cryptomelane (Table 1). The original material contained much water and some Fe, besides other impurities.

(b) A newly purchased reagent from Mallinckrodt, much purer according to the label, was pyrolusite to start with and did not form cryptomelane before inversion to Mn_2O_3.

(c) The analysis of a reagent from General Chemical Co. after heating 20 hours at 300°C., is given in Table 2. It gave a cryptomelane pattern to begin with and a slightly better one after heating 20 hours at 300°C. If this material is heated to 500°C. for 20 hours, the pattern of Mn_2O_3 (bixbyite) is superimposed on that of cryptomelane. It is thought that all of the material probably would invert if heated a longer period.

TABLE 2. CHEMICAL COMPOSITION OF REAGENT OF "GENERAL CHEMICAL CO." AFTER HEATING 20 HOURS AT 300°C.

(Cryptomelane)

Chemical Composition		*Mol. Ratio*
MnO_2	84.93	.9770
MnO	7.33	.1033
Fe_2O_3	.10	.0006
Na_2O	.10	.0016
K_2O	3.10	.0329
H_2O+	2.22	.1232
H_2O-	1.70*	.0943
Analyst—R. B. Ellestad	99.48	

* Water absorbed in less than 24 hours after cooling. The H_2O content as the material comes from the bottle is 16.91%. This is lost as follows:

110°C.	12.62%
300°	15.44
400°	16.10
475°	16.85

The reagent also contains traces of SO_4 and insolubles in HCl.

(d) When $KMnO_4$ is treated with HCl in a boiling solution and NH_4OH is added in sufficient amounts to keep the solution almost neutral, an amorphous precipitate forms which on heating to 400°C. gives cryptomelane.

(e) When electrolytic Mn (99.9% pure) is dissolved in concentrated HNO_3 and this solution is oxidized with $KClO_3$ while boiling, the resulting precipitate was pyrolusite in one experiment. In another, amorphous material resulted which on heating to 400°C. gave cryptomelane. These behaviors of precipitated oxides or hydroxides show that the "histories" of the compounds influence the resulting structures.

One of the most interesting findings is that hollandite is isostructural with cryptomelane, as shown by the patterns of Table 1. Since Frondel and Heinrich (5) have shown that hollandite has the same structure as coronadite, an attempt will be made to derive a formula for cryptomelane and hollandite which in turn is based on that of coronadite.

CHEMICAL COMPOSITION

In the earlier attempts to arrive at a formula for psilomelane it was not possible to be sure of the homogeneity of the analyzed specimens. Some of them probably were mixtures. The first analyses checked by x-ray powder spectra are by Vaux (4). He arrives at the following formula for Ba-psilomelane: $H_4R_2Mn^4_8O_{20}$, where R stands for Mn^2, Ba, Mg, Ca, Ni, Co, and Cu. Since Mn^2 and Ba are each about equal to 1, except in one of his analyses, he could have written the formula also $H_4Mn^2BaMn^4_8O_{20}$. The Ba ion is so much larger than the Mn^2 that it probably does not "trade places" with it in the structure. The observed density of this material is in fair agreement with the theoretical content of the unit cell as shown by Vaux.

This does not seem to be the case with coronadite for which Frondel and Heinrich (5, p. 55) have given the formula $MnPbMn_6O_{14}$ or $MnPbMn_6O_{14} \cdot H_2O$. By their own calculations the content of the unit cell based on the mean of two analyses is, however, $Mn_{.97}Pb_{1.17}Mn_{6.31}O_{15.51}(H_2O)_{.73}$, and the observed density would correspond to this formula. The densities for the two theoretical formulas above would be 4.87 and 4.98, respectively. They are too low by about 10 per cent, which in view of the fact that theoretical densities are usually higher than observed ones, throws doubt on the validity of these formulas. The dimensions of the body-centered pseudotetragonal unit cells are:

Coronadite	$a_0=6.95$ Å,	$c_0=5.72$ Å.	Volume $=276.2$ Å^3
Hollandite	$=6.94$	5.71	275.0
Cryptomelane	$=9.82$	2.86	275.8

The relationship between the two cells is simple: $6.95 \times \sqrt{2} = 9.82$. The horizontal edge of the unit cell of cryptomelane is the same as the diagonal of the base of coronadite. It may be assumed that the distribution of the O ions in the two cells are identical, if not that of all of the atoms or ions. Another significant observation is that the value of c_0 of these cells ($c_0/2$ for coronadite and hollandite) is like c_0 in pyrolusite (polianite). It was pointed out by Vaux (4, p. 526) that Ba-psilomelane has the same c_0 as pyrolusite and that manganite is twice as large (5.74). One is tempted to conclude that these minerals are constructed similarly parallel to the c axis, as is also suggested by their fibers parallel to c.

In Table 3 the three isostructural minerals for which chemical and x-ray analyses are available have been recalculated on the basis that the oxygen content of the unit cell is 16. This number of O ions has been chosen because then the observed densities of the specimens of Table 3 agree best with the theoretical ones. Also, pyrolusite with the same height of unit cell has 16 O ions, provided $a_0=4.38$ Å is doubled. This comparison can also be extended to manganite which for a unit cell twice as high and a corresponding doubling of its a_0 and b_0 dimensions contains 32 O ions. These facts are too striking as to be without significance.

The hollandite from Balaghat, India, described by Fermor (9, pp. 92 and 93) has been included in Table 3. Though no x-ray spectrogram of this specimen is available, there is little doubt but that it is hollandite.

TABLE 3. CALCULATED ATOMIC CONTENTS AND DENSITIES OF UNIT CELLS BASED ON 16 OXYGENS IN A CELL

Si, Ca, and Mg omitted

	Cryptomelane[1]				Crypt.[3] Artificial	Coronadite[5]		Hollandite[2]	
	1	2	3	4		5	6	Kajlidongri	Balaghat
Mn^{4}	7.39	7.53	7.16	7.57	7.47	6.72	6.70	6.28	6.78
Mn^{2}	.22	.42	.37	.26	.79	1.11	.96	.60	1.00
Cu	.01	.04	.01	—					
Co	—	.02	.02	.01					
Zn	.49	—	—	.16			.01		
Al	.05	—	.20	.06		.02	.13	.15	.19
Fe	.05	.02	.38	.01		.07	.13	1.10	.43
Ba	.01	.05	—	—		.01		.95	.15
Sr	—	.02	—	—					
Pb	—	—	—	—		1.26	1.23		
K	.57	.62	.62	.50	.50				.55
Na	.11	.11	.14	.12	.02				.14
$\Sigma +$ ions	8.90	8.83	8.90	8.69	8.78	9.19	9.16	9.08	9.24
Mol. W.	736	734	724	721	730	952	942	830	762
Theor. Density	4.40	4.39	4.33	4.31	4.37	5.68	5.63	4.96	4.56
Sp. Gravity	4.33	4.32	4.41	4.17	n.d.	5.44	5.25[4]	4.95	4.59
H_2O+	1.10	.71	1.47	1.50	.94–1.66	.98	.58	none	.48

[1] Chemical analyses and specific gravities of these four in paper by Richmond and Fleischer (3).

[2] Analyses in Fermor (9, pp. 91 and 93).

[3] Artificial cryptomelane of Table 2.

[4] Low on account of 7% insolubles (Lindgren and Hillebrand).

[5] Analyses in paper by Frondel and Heinrich (5).

The O of the H_2O of the analyses has been omitted from the 16 O positions in the calculations for the following reasons:

1. Practically all H_2O can be driven off without causing a collapse of the structure. The exact temperature when all H_2O is gone cannot be determined on account of the inversion to Mn_2O_3, at about 500°C. for the material of Table 2.

2. The H_2O_+ content is extremely variable in the three isostructural minerals, approaching zero in hollandite from Kajlidongri. This is shown in the bottom row of Table 3.

3. The artificial cryptomelane of Table 2 absorbs again a part of the water as follows:

After heating to 110°	a trace
After heating to 300°	2.8–3.00%
After heating to 400°	2.3–2.7%
After heating to 475°	2.2%

The rate and amount of absorption differ somewhat depending apparently on the humidity of the atmosphere. It is, however, quite rapid and a matter of only a few hours for the bulk of the H_2O. Natural cryptomelane behaves similarly but much more slowly, depending upon its physical condition. The absorption is only 10 per cent of the total H_2O lost of the specimen from Romanèche. The H_2O content of these crystals is only about 1.2 per cent.

Since this H_2O in a massive specimen (see those of Richmond and Fleischer, 3) cannot be just adsorbed on the surface, one must conclude that it occupies positions large enough for H_2O molecules. It would be like zeolitic water. Positions large enough for K, Ba, and Pb ions would also be able to accommodate H_2O.

At first glance there seems to be no order in the number and distribution of the cations. The sum of them approaches 9 in all of the species. If we arrange them by sizes, we find no agreement either. It has been stated frequently that these minerals are manganates. The Mn^6 ion has a radius of about 0.35 Å while those of Mn^4, Mn^3, and Mn^2 are about 0.52, 0.70, and 0.90, respectively. Mn^6 has tetrahedral coordination while the others have an octahedral one. Such ions as Zn, Cu, Co, Al, and Fe can substitute in the octahedral positions. Na could either be octahedral or, as is assumed here, go with K. Since the unit cell of the structure is small, it must be assumed that the number of different atomic positions is small. The complexity of the formula is not a real structural one, but is caused by the numerous possible substitutions. These substitutions, including Mn ions of different sizes, cause distortions in the lattice which prevent the growth of relatively large and distinct crystals. The only direction in which these strains do not hinder growth materially seems to be parallel to the *c* axis. Fibers are the result in the better developed cryptomelanes and particularly in hollandite and coronadite where higher temperatures may have produced an "annealing" effect.

The ions of Ba, Pb^{++}, and K are of very similar sizes and their substitution, one for another, may be taken for granted. It is, however, strange that only about half as many K ions enter the structure as Pb or Ba ions. The explanation for this behavior must be sought in the state of oxidation of the Mn. If most of the Mn is present as Mn^4 (as stated commonly in analyses), the 32 negative charges of the structure are practically used up, and K can go into the structure to a very limited extent; "holes" are left. This would be common under oxidizing conditions near the surface of the ground. On the other hand, where considerable Mn is of a lower valence, divalent cations of Ba or Pb, depending upon which are available, could enter the same positions.

A number of experiments were performed to investigate this behavior further. Three portions of the artificial material of Table 2 (heated originally to 300°C.) were boiled in solutions of $AgNO_3$, $BaCl_2$, and $Pb(NO_3)_2$ for about 24 hours. After many careful washings and drying at 300°C. for 6 hours, their analyses, converted to oxides, showed the following: 14.68 Ag_2O, 6.01 BaO, 11.84 PbO. If the metals went into the unit cell as ions, they would occupy 1.00, 0.29, and 0.41 positions, respectively. This calculation can be made only if it is assumed that the composition of the cryptomelane remains the same except for the replacement of the K ions by the metals. Analyses for the H_2O+ and H_2O- were remarkably similar for the three samples, and much like the original material. In other words, about 3 per cent of H_2O was regained within 3 hours in a steam-heated laboratory. Qualitative tests for K showed that some had gone into solution, some remained in the treated material.[1] The solutions containing the Ag or Pb salts had a *p*H of about 2.5 and that of Ba, a *p*H of 4.[2] Mn was found qualitatively in the first two solutions. The samples treated with Ag or Ba were dark brown in color like the original, that of Pb was very dark gray, practically black. The following conclusions were drawn from these experiments:

Only a part of the K ions is replaced by the new metals. There must be open positions in the structure into which the other metal ions can go. Some ions may be just adsorbed. The fact that Ag is taken up in much larger quantities than Ba or Pb must be partly due to its monovalence, partly possibly to its smaller radius. One other possibility exists, that a part is changed to metallic silver by the action of the Mn^{++} ions. The radius of a silver atom is 1.4 Å. As an atom it would fit into the same positions in which the zeolitic water is stored. There is no doubt, at least in the case of Ba and Pb, that some of the Mn of higher valence must be reduced to a lower state in order to maintain electrostatic balance.

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[1] Due to the present emergency no other quantitative work was possible.

[2] Pyrolusite of extremely fine grain does not show any of these behaviors when treated the same way.

Conclusions

Cryptomelane, hollandite, and coronadite are isostructural and form isomorphous mixtures to some extent. It is thought that the mixing might be more complete if the solutions from which the minerals form contained the necessary elements in the proper proportions. In other words, if Pb or Ba had been present in considerable concentrations when cryptomelane was forming, these elements could have occupied the K positions, in the structure. The state of oxidation of Mn is important in this connection and controls the ratios $x:y:z$ in the formulas below.

The unit cell of the structure contains 16 O ions. This number gives the best agreement between observed and theoretical densities. There are also structural reasons that suggest this number. The formula which includes all the members of the group is as follows:

$$Mn^4{}_{8-(x/2+y/4+z/2)}(Mn^2,\ R^2)_x(K,\ Na)_y(Ba,\ Pb)_zO_{16}\cdot(H_2O)_{2-(y+z)}$$

The members could then have the following formulas:
Average of four cryptomelanes of Table 3:

$$Mn^4{}_{7.42}(Mn^2,\ R^2)_{.81}(K,\ Na)_{.70}Ba_{.02}O_{16}\cdot(H_2O)_{1.31}$$

Average of two hollandites of Table 3:

$$Mn^4{}_{6.53}(Mn^2,\ R^2)_{2.20}(K,\ Na)_{.34}Ba_{.55}O_{16}\cdot(H_2O)_{1.13}$$

Average of two coronadites:

$$Mn^4{}_{6.71}(Mn^2,\ R^2)_{1.30}(Pb,\ Ba)_{1.25}O_{16}\cdot(H_2O)_{.75}$$

R^2 includes the elements Cu, Co, Zn, Al, and Fe. The trivalent Al and Fe have been included under R^2. Allowance must be made for this when x is computed. H_2O given off above 110°C. is present as molecular H_2O filling positions which could be occupied by K, Ba, or Pb, except for electrostatic balance. The total possible amount of H_2O as given in the formulas above is, therefore, determined by the percentage of K, Ba, and Pb in the structure. The actual amount of H_2O comes close to this figure except in hollandite. The water is zeolitic in nature since a part of it at least is reabsorbed after cooling.

Mn designated as Mn^4 in the formula may be partly Mn^6 in which case it would have fourfold coordination and probably occupy different positions from those of Mn of lower valence. It is more likely, however, that all Mn has six coordinates and that its highest chemical valence is 4, as in pyrolusite and other manganese minerals. This would result in a simpler structure which is more likely in the relatively small unit cell. Even then so many substitutions occur in the structures that in most of them considerable strains are set up resulting only in microscopic crystalline aggregates. The temperatures and pressures of formation have some influence on this behavior. Hollandite, for example, is formed under conditions approaching metamorphism. It is lower in H_2O. Cryptomelane from Romanèche is of hydrothermal origin. Both occur as individual crystals. Cryptomelane can be produced synthetically. This product, as well as natural cryptomelanes, breaks down at about 500°–540°C. Cubic Mn_2O_3 (bixbyite) is one of the results. The occurrence of a well crystallized cryptomelane, probably the original romanechite of Lacroix, at Romanèche, France, is established.

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RESETTING A TRICLINIC UNIT-CELL IN THE CONVENTIONAL ORIENTATION

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Introduction

The rules for the conventional orientation of a triclinic crystal (Donnay and Mélon, 1933; Donnay, Tunell, and Barth, 1934; Donnay, 1943) are the following. The axes must be: (1) chosen along the shortest three translations; (2) named so as to satisfy the condition $c<a<b$; (3) oriented so that the axial cross is right-handed, with α and β both obtuse.

The first of these rules has been followed generally in the past, so that the problem of reorienting a triclinic crystal usually reduces to resetting the unit-cell, that is to say, renaming and reorienting the axes. Although this problem admits of a straightforward solution, it is encountered so often in crystallographic work that its treatment at this place should be of practical value.

Resetting a Triclinic Cell

The original axial elements are usually given in the form (right-handed axial cross):

$a_0=7.88$	$b_0=7.27$	$c_0=7.03$
$\alpha=89°59'$,	$\beta=95°16'$,	$\gamma=103°25'$,

Copy them, without the letters, as follows:

7.88,	7.27,	7.03
89°59′,	95°16′,	103°25′.

Relabel the axes c, a, b, in increasing order (so as to satisfy the condition $c<a<b$). The new labels of the interaxial angles are thereby determined (respectively: γ, α, β). Thus:

$b=7.88$	$a=7.27$,	$c=7.03$,
$\beta=89°59'$,	$\alpha=95°16'$,	$\gamma=103°25'$.

Two cases may occur: The arrangement of letters, read from left to right, either is or (as in the above example) is not a cyclic permutation of *a b c*.

I. If the arrangement is one of the three cyclic permutations (*a b c*, *b c a*, *c a b*), the axial cross has remained a right-handed one. If a reorientation of the axes is found to be necessary in order to comply with the convention "α and β both obtuse," two axes must change their signs in order that the axial cross remain right-handed.

Any one of four possibilities may arise: (1) α and β both obtuse; (2) α obtuse, but β acute; (3) β obtuse, but α acute; (4) α and β both acute.

(1) α and β both obtuse.—No further modification of the setting is needed.

(2) α obtuse, β acute.—A reorientation of axes is necessary to make the angle β obtuse. As two axes must be reversed, only one of the three interaxial angles can retain its character (obtuse or acute), namely, the angle comprised between the two axes that change their signs. Since α must remain obtuse, the axes to be reversed are *b* and *c*. After this transformation, β has changed from acute to obtuse (as desired), and γ has also changed its character (which is immaterial).

(3) β obtuse, α acute.—This case is similar to the one just considered. Reverse the signs of *a* and *c;* take the supplements of α and γ.

(4) α and β both acute.—The only angle that should retain its character (obtuse or acute) is γ. Reverse the signs of *a* and *b;* take the supplements of α and β.

II. If the arrangement of letters, obtained after renaming the axes, is not a cyclic permutation of *a b c*, but is one of the other three permutations (*a c b*, *c b a*, *b a c*), the axial cross has become left-handed. A reorientation of the axes is imperative in any case in order to restore the right-handed character of the axial cross; it may also be needed to bring the new setting into agreement with the rule "α and β both obtuse." The left-handed axial cross can be made right-handed in two ways only: either by changing the sign of a single axis, or by reversing all three axes.

The four possibilities to be examined are the same as before:

(1) α and β both obtuse.—Reverse all three axes. The axial cross again becomes right-handed. All interaxial angles keep the same values.

(2) α obtuse, β acute.—Reversing one axis only changes the character (obtuse or acute) of the two angles which this axis makes with the other two axes. The angle α cannot be changed; β must, and γ may, become obtuse. Reverse the sign of *a*; take the supplements of β and γ.

(3) β obtuse, α acute.—For the foregoing reasons, reverse the sign of *b*; take the supplements of α and γ.

(4) α and β both acute.—Change the sign of *c*; take the supplements of α and β.

The above discussion is summarized in a double-entry table (Table 1), which also gives the old-to-new transformation matrices for the 24 possible right-handed settings. This table should prove worthwhile as a labor-saving device, whenever a large number of triclinic cell reorientations are to be performed. The procedure is simple: rename the axes so that $c<a<b$; if, after renaming the axes, α and β are both acute, take

their supplements; if only one of them is acute, take its supplement and also that of γ; the old-to-new transformation matrix is then found in the table.

EXAMPLES

The triclinic species given in Wyckoff (1931, 1935) have been worked out as examples. In each case it has been assumed that the unit lengths were the shortest three translations. The examples are listed in groups, each under the appropriate transformation, indicated by its letter (cp. Table 1).

These examples probably constitute a representative sampling of the various types of setting used for triclinic crystals. They are instructive in providing a statistical survey and they also bring out certain special cases which require additional conventions.

If one of the two interaxial angles α and β is 90° (as in pectolite and wollastonite), two settings are found, as 90° is considered obtuse or acute in turn (transformations W and X, respectively). That setting which leads to γ obtuse is obviously the more desirable.

If both α and β are 90° (as in $3KPbCl_3 \cdot H_2O$), two sets of axial elements are likewise obtained, with supplementary values for γ (transformations O or R, and P or Q). Again the setting that makes γ obtuse should be preferred.

A case where $a=b$ has been encountered (H_3BO_3). Two settings are obtained (transformations A and W), which differ from each other by the interchange of α and β. To cope with such cases (which seldom occur), an additional convention may be devised (α smaller than β, for instance), although refinement of the measurements will usually reveal a difference between the unit lengths.

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TABLE 1. TRANSFORMATION MATRICES
(Old setting to new setting)

After renaming the axes:	In order to satisfy the condition $c<a<b$, the original $a_0b_0c_0$ become:					
	abc	*bca*	*cab*	*acb*	*cba*	*bac*
α and β both obtuse: Leave all angles un-unchanged	A $\begin{matrix}1&0&0\\0&1&0\\0&0&1\end{matrix}$	E $\begin{matrix}0&1&0\\0&0&1\\1&0&0\end{matrix}$	K $\begin{matrix}0&0&1\\1&0&0\\0&1&0\end{matrix}$	O $\begin{matrix}\bar{1}&0&0\\0&0&\bar{1}\\0&\bar{1}&0\end{matrix}$	S $\begin{matrix}0&0&\bar{1}\\0&\bar{1}&0\\\bar{1}&0&0\end{matrix}$	W $\begin{matrix}0&\bar{1}&0\\\bar{1}&0&0\\0&0&\bar{1}\end{matrix}$
α obtuse, β acute: Take supplements of β and γ	B $\begin{matrix}1&0&0\\0&\bar{1}&0\\0&0&\bar{1}\end{matrix}$	F $\begin{matrix}0&1&0\\0&0&\bar{1}\\\bar{1}&0&0\end{matrix}$	L $\begin{matrix}0&0&1\\\bar{1}&0&0\\0&\bar{1}&0\end{matrix}$	P $\begin{matrix}\bar{1}&0&0\\0&0&1\\0&1&0\end{matrix}$	T $\begin{matrix}0&0&\bar{1}\\0&-1&0\\1&0&0\end{matrix}$	X $\begin{matrix}0&\bar{1}&0\\1&0&0\\0&0&1\end{matrix}$
β obtuse, α acute: Take supplements of α and γ	C $\begin{matrix}\bar{1}&0&0\\0&1&0\\0&0&\bar{1}\end{matrix}$	G $\begin{matrix}0&\bar{1}&0\\0&0&1\\\bar{1}&0&0\end{matrix}$	M $\begin{matrix}0&0&\bar{1}\\1&0&0\\0&\bar{1}&0\end{matrix}$	Q $\begin{matrix}1&0&0\\0&0&\bar{1}\\0&1&0\end{matrix}$	U $\begin{matrix}0&0&1\\0&\bar{1}&0\\1&0&0\end{matrix}$	Y $\begin{matrix}0&1&0\\\bar{1}&0&0\\0&0&1\end{matrix}$
α and β both acute: Take supplements of α and β	D $\begin{matrix}\bar{1}&0&0\\0&\bar{1}&0\\0&0&1\end{matrix}$	H $\begin{matrix}0&\bar{1}&0\\0&0&\bar{1}\\1&0&0\end{matrix}$	N $\begin{matrix}0&0&\bar{1}\\\bar{1}&0&0\\0&1&0\end{matrix}$	R $\begin{matrix}1&0&0\\0&0&1\\0&\bar{1}&0\end{matrix}$	V $\begin{matrix}0&0&1\\0&1&0\\\bar{1}&0&0\end{matrix}$	Z $\begin{matrix}0&1&0\\1&0&0\\0&0&\bar{1}\end{matrix}$

LIST OF EXAMPLES

Transformation and Substance	Old Setting			New Setting
(A) Albite, $NaAlSi_3O_8$	8.14	12.86	7.17	
	94° 3′	116°29′	88° 9′	
Calcium sulfate urea, $CaSO_4 \cdot CO(NH_2)_2$	14.74	14.95	6.47	
	91°26′	90°22′	86°42′	
4 Nitro-2-Methylaminotoluene, (red form)	7.6	8.5	7.5	
	113°	98°	109°	
Aenigmatite	18.3	18.3	10.6	
	96°30′	96°30′	113°30′	
Kyanite, Al_2SiO_5	7.09	7.72	5.56	
	90° 5′	101° 2′	105°44′	
Ammonium hydrogen fumarate, $C_4H_7NO_4$	7.00	7.44	6.56	
	107° 1′	117°58′	69°16′	
Fumaric acid	7.60	15.11	6.61	
	90°40′	111° 5′	89°48′	
Boric acid, H_3BO_3	7.04	7.04	6.56	
	92°30′	101°10′	120°	
Celsian[1]	8.63	13.10	7.29	
	ca. 90°	116°	ca. 90°	
Andesine	8.14	12.86	7.17	
	93°23′	116°28′	89°59′	
Tungstic trioxide[2] WO_3	7.28	7.48	3.82	
	ca. 90°	ca. 90°	ca. 90°	

LIST OF EXAMPLES—*Continued*

Transformation and Substance	Old Setting			New Setting		
(B) Stilbene+2 mol. 1,3,5 Trinitrobenzene,	12.7	15.4	7.7	12.7	15.4	7.7
$C_6H_5CH{=}CHC_6H_5 \cdot 2[C_6H_3(NO_2)_3]$	102°16′	85°30′	87°35′	102°16′	94°30′	92°25′
(C) Copper sulfate pentahydrate,	6.07	10.78	5.89	6.07	10.78	5.89
$CuSO_4 \cdot 5H_2O$	82° 5′	107° 8′	102°41′	97°55′	107° 8′	77°19′
Rhodonite, $Mn_4Ca(SiO_3)_5$	7.77	12.45	6.74	7.77	12.45	6.74
	85°10′	94° 4′	111°29′	94°50′	94° 4′	68°31′
Racemic acid (anhydrous),	7.18	9.71	4.98	7.18	9.71	4.98
$COOH(CHOH)_2COOH$	82°20′	118° 0′	72°58′	97°40′	118° 0′	107° 2′
Racemic acid monohydrate, $C_4H_4O_6 \cdot H_2O$	8.09	10.03	4.81	8.09	10.03	4.81
	76° 2′	96°57′	120° 8′	103°58′	96°57′	59°52′
(D) Thallium mesotartrate, $Tl_2C_4H_4O_6$	13.26	16.12	7.63	13.26	16.12	7.63
	75°54′	86°37′	82°14′	104° 6′	93°23′	82°14′
Cholesteryl salicylate, $C_{34}H_{50}O_3$	9.68	12.52	6.31	9.68	12.52	6.31
	85°53′	77°41′	84° 1′	94° 7′	102°19′	84° 1′
(E) No example found						
(F) Hexamethyl benzene, $C_6(CH_3)_6$	9.01	8.92_6	5.34_4	8.92_6	9.01	5.34_4
	44°27′	116°43′	119°34′	116°43′	135°33′	60°26′
(G) Bisethylene diamino platinous chloride,	8.37	4.95	6.86	6.86	8.37	4.95
Pt $(C_2H_8N_2)_2Cl_2$	100°46′	111°40′	81°56′	98° 4′	100°46′	68°20′
Racemic methyl ephedrine hydroiodide,	11.2	7.67	7.68	7.68	11.2	7.67
$C_{11}H_{17}ON \cdot HI$	108°55′	95°36′	84°15′	95°45′	108°45′	84°24′
(H) Cyclododecane, $C_{12}H_{24}$	7.84	5.44	7.82	7.82	7.84	5.44
	98°18′	64°	81°	99°	98°18′	64°
(K) Anorthite, $CaAl_2Si_2O_8$	8.21	12.95	14.16	12.95	14.16	8.21
	93°13′	115°56′	91°12′	115°56′	91°12′	93°13′
(L) Labradorite	8.21	12.95	14.16	12.95	14.16	8.21
	93°21′	116° 3′	89°55′	116° 3′	90° 5′	86°29′
Babingtonite	6.73	7.54	12.43	7.54	12.43	6.73
	112°22′	93°48′	86° 9′	93°48′	93°51′	67°37′
(M) (N) No example found.						
(O) Potassium lead chloride hydrate,[3]	14.35	9.05	14.50	14.35	14.50	9.05
$3KPbCl_3 \cdot H_2O$	ca. 90°	113°	ca. 90°	ca. 90°	ca. 90°	113°
(P) Sodium iodide dihydrate, $NaI \cdot 2H_2O$	6.85	5.76	7.16	6.85	7.16	5.76
	98°	119°	68½°	98°	111½°	61°
p-Cyano-o-Nitro-p′-Methoxystilbene,	8.50	7.45	13.35	8.50	13.35	7.45
$C_6H_3(CN)(NO_2)CH{=}CHC_6H_4(OCH_3)$	98° 6′	106°20′	75°40′	98° 6′	104°20′	73°40′
Potassium mesotartrate dihydrate,	7.02	6.90	11.02	7.02	11.02	6.90
$K_2C_4H_4O_6 \cdot 2H_2O$	95°44′	102°52′	61°46′	95°44′	118°14′	77° 8′
(Q) α-Potassium dichromate, $K_2Cr_2O_7$	7.50	7.38	13.40	7.50	13.40	7.38
	82° 0′	96°13′	90°51′	98° 0′	90°51′	83°47′
(R) 2,7 dinitroanthraquinone fluorene,	8.2	7.4	19.0	8.2	19.0	7.4
$C_{14}H_6(NO_2)_2O_2$, $(C_6H_4)_2CH_2$	78°	82°	ca. 80°	102°	ca. 100°	82°
(S) Potassium persulfate, $K_2S_2O_8$	5.11	6.51	5.48	5.48	6.51	5.11
	96°45′	90°10′	95°15′	95°15′	90°10′	96°45′
Copper sulfate pentahydrate[4]	5.12	10.7	5.97	5.97	10.7	5.12
$CuSO_4 \cdot 5H_2O$	82°16′	107°26′	102°40′	102°40′	107°26′	82°16′
(T) (U) (V) No example found						
(W) Pectolite, $NaHCa_2(SiO_3)_3$	7.91	7.08	7.05	7.08	7.91	7.05
	90°	95°10′	103° 0′	95°10′	90°	103° 0′
Wollastonite, $CaSiO_3$	7.88	7.27	7.03	7.27	7.88	7.03
	90°	95°16′	103°25′	95°16′	90°	103°25′
Malonic acid, $CH_2(COOH)_2$	8.36	5.33	5.14	5.33	8.36	5.14
	94°56′	103°56′	71°30′	103°56′	94°56′	71°30′
(Y) (Z) No example found						

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[1] Transformation C leads to the same axial elements as transformation A.

[2] Transformations A, B, C, and D lead to the same results.

[3] Transformation R would lead to the same results.

[4] Example of a redetermination that changes the setting.—Compare transformation C.

FIBROUS SEPIOLITE FROM YAVAPAI COUNTY, ARIZONA

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Abstract

Data yielded by chemical, optical, and x-ray methods of analysis identifies a hydrous magnesium silicate from Yavapai County, Arizona, as fibrous sepiolite. The study of this specimen is of interest because of the further information it yields concerning the nature of sepiolite. The literature may profit from more coordinated chemical, optical, and x-ray data on this mineral. The term 'parasepiolite' is justified rather than sepiolite when referring to the fibrous, highly crystalline variety of this material. A rather complete bibliography of sepiolite is included, in addition to the references cited.

Occurrence

The hydrous magnesium silicate described herein occurs in a contact zone situated about a half mile south of the Santa Maria River near the western boundary of Yavapai County and about 40 miles, by road, in a westerly direction from Congress Junction, Arizona.

This locality, in southwestern Yavapai County, is in the ruggedly dissected basin of the Santa Maria River west of the McCloud Mountains, a granite range that attains a height of 4900 feet. The region is composed mainly of granite, gneiss, and schist intruded by various dikes and stocks and overlain in places by mesa-forming lavas.

This deposit was prospected thoroughly by the R. T. Vanderbilt Co., New York, but was found to be too limited in extent for commercial development.

Physical Properties

In a hand specimen this material is white, massive, and compact with a foliated structure. The surface is smooth with a dull luster that assumes a polish with slight rubbing.

The material was studied optically by the immersion method and in thin section, being found homogeneous and free from noticeable impurities. It is completely crystalline without any indication of an 'amorphous' constituent.

In thin section, with plain light, little detail can be seen because of the low relief in balsam and lack of color. Under crossed nicols, however, the truly fibrous structure, similar to serpentine, is made evident. The fibers show a wavy extinction which is essentially parallel to the length, with positive elongation. The birefringence is low and the interference figure is negative, $2V =$ about 40°–60°.

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The fragments are irregular in outline but have a fibrous structure. The refractive indices are: $\alpha=1.490$, $\gamma\simeq1.505$ ($\pm.003$). These values agree with those given by Larsen and Berman (1934) for parasepiolite (fibrous), namely: $\alpha=1.498$, $\gamma=1.506$. The indices reported by Daly (1935) for fibrous sepiolite are given as $\alpha=1.506$, $\gamma=1.526$, and the type material from Madagascar (Caillere 1933) has a mean index of 1.499.

A comparison of the optical properties of several sepiolites is given in Table 1.

Table 1. Optical Properties of Sepiolite

Specimen	Color	Extinction	Elongation	Indices		Optic Sign	Axial Angle
				α	γ		
(1)	white	parallel	positive	1.490	1.505	neg.	2V=40°–60°
(2*a*)	white	parallel	positive	1.498	1.506	neg.	2V=50°
(2*b*)	white	parallel	positive	1.519	1.526	neg.	—
(3)	white	parallel	positive	1.506	1.526	neg.	—
(4)	white	parallel	positive	1.499		—	—
(5)	gray	parallel	positive	1.531		—	—

(1) Hydrous magnesium silicate, Yavapai Co., Arizona.
(2*a*) Fibrous sepiolite, Larsen and Berman (1934).
(2*b*) Sepiolite, Larsen and Berman (1934).
(3) Fibrous sepiolite, Daly (1935).
(4) Fibrous sepiolite, Mlle. Caillere (1933).
(5) Fibrous sepiolite, W. H. Bradley (1930).

General Description of Sepiolite

Physically sepiolite is usually described as a white or grayish-white material, compact, with a smooth feel and a fine clay-like texture. Microscopically it seems to be a mixture of a fine fibrous material and an 'amorphous' substance of apparently the same composition. The fibrous material is called alpha or parasepiolite and the 'amorphous' component beta sepiolite.

Daly (1935) describes sepiolite from Crestmore, California, as a white fibrous material. Optically it is composed of finely interlocking fibers that have extinction parallel to the length and refractive indices of $\alpha=1.506$ and $\gamma=1.526$. The chemical formula is given as $2MgO\cdot3SiO_2\cdot3H_2O$, with variable water content.

Mlle. Caillere (1933) in describing a fibrous sepiolite from Madagascar indicates that the material is white with a fibrous texture. It has low birefringence, extinction parallel to the length of the fibers, positive elongation, and a mean refractive index of 1.499. Its chemical formula is $2MgO \cdot 3SiO_2 \cdot 4H_2O$.

Sepiolite or meerschaum, as it is known commercially, was first discovered in this country in Grant County, New Mexico (Bush 1915) early in 1875. However, no meerschaum has been produced in the United States since about 1914. The deposits of Eskishehir, in Anatolia, Asia Minor, were the principal source for over a century before this discovery and to this date still supply most of the world's demands (*Minerals Yearbook* 1940). Other commercial deposits are reported in Greece, on the Island of Euboea; in Moravia, Austria; in Spain near Vallecas, Madrid and Toledo; and in Morocco (Sterrett 1907).

Meerschaum was formerly used almost exclusively in the manufacture of smokers' articles. It is now, however, being used as a light weight building material in Spain, elsewhere as a soap substitute, and as a constituent of porcelain ware. According to Dr. Manfred Kraemer (1939) of Newark, New Jersey, magnesium trisilicate (sepiolite) has recently found use, in England and in this country, as a medicament.

CHEMICAL CONSIDERATIONS

Published chemical analyses of sepiolite occur infrequently throughout the literature. In France Mlle. Caillere (1933, 1934), M. Migeon (1936), and M. Longchambon (1937) have recorded a few analyses but most of their efforts have been devoted to hydrothermal studies. In this country W. T. Schaller (1936), Wm. F. Foshag (1928), Douglas Sterrett (1907), and W. H. Bradley (1930) have listed analyses of this mineral.

The relationship between the chemical composition of the hydrous magnesium silicate from Yavapai County and those described by the above authorities is given in Table 2.

TABLE 2. CHEMICAL ANALYSES OF SEPIOLITE

	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	$H_2O(-)$	$H_2O(+)$	Total
(1)	54.83	0.28	0.45	0.55	24.51	0.35	0.03	8.18	10.74	99.92
(2)	53.10	0.32	1.56	1.27	24.87	—	—	8.42	10.11	99.65
(3)	54.76	0.33	—	—	25.15	—	—	20.17		100.41
(4)	54.37	—	0.98	0.59	24.13	—	—	9.41	10.19	99.67
(5)	54.4	—	—	—	24.4	—	—	8.9	12.3	100.00
(6)	55.34	1.81	0.43	0.24	22.95	—	—	8.60	10.20	99.57
(7)	50.4	—	0.5	1.4	22.5	—	—	24.95		99.75
(8)	57.10	0.58	—	0.17	27.16	—	—	14.78		99.79
(9)	58.40	1.86	—	0.42	26.58	—	—	11.86		99.31*

* Included in this total are TiO_2 0.10% and CO_2 0.69%.
(1) Hydrous magnesium silicate, Yavapai County, Arizona.
(2) Fibrous sepiolite, Madagascar; Mlle. Caillere (1933).
(3) Sepiolite, Dorsey Mine; M. Migeon (1936).
(4) Sepiolite, Coulommiers; Mlle. Caillere (1933).
(5) Magnesium trisilicate (sepiolite) (Macksoud 1939).
(6) Sepiolite, Durango, Mexico; Wm. F. Foshag (1928).
(7) Magnesium trisilicate (sepiolite); Surfleet and Porter (1940).
(8) Sepiolite, New Mexico; Douglas Sterrett (1907).
(9) Sepiolite, Utah; W. H. Bradley (1930).

The silica, magnesia and water content of the analyses demonstrate an apparent similarity. In a consideration of the chemical composition of sepiolite interest is usually focussed on the magnesia–silica ratio. According to Surfleet and Porter (1940) a true magnesium trisilicate (sepiolite) should have a gravimetric ratio of magnesia to silica equivalent to 1:2.24, the allowable limits being between 2.21–2.28. A value of 2.24, identical with the theoretical, was calculated for the Yavapai County mineral. The ratio for sepiolite, free of impurities, is diagnostic of the correct constitutional formula.

The similarity of the water content is also significant. There seems to be a divergence of opinion throughout the literature on the number of water molecules contained in the sepiolite structure. The fibrous variety, known as alpha or parasepiolite, is thought to contain four molecules of water and the so-called 'amorphous' or beta form is thought to contain two molecules of water. Schaller (1936) made a careful study of this particular question and has offered the following explanation: out of 56 chemical analyses of sepiolite, 34 had the water content of alpha sepiolite (four molecules), 15 had the water content of beta sepiolite (two molecules), and 7 were intermediate. It was, however, subsequently found that the specimens with the low water content had been heated in varying degrees, some as high as 200°C., before analysis. These analyses were recalculated and all but four agreed with the alpha form of four molecules of water. This seems to indicate that there is actually only one type of sepiolite and it contains four molecules of water.

The formula of the Yavapai County specimen, as calculated from the chemical analysis, is $2MgO \cdot 3SiO_2 \cdot 4H_2O$ corresponding to the formula assigned to sepiolite and substantiated by Schaller (1936), Mlle. Caillere (1933), M. Longchambon (1935), and others.

X-RAY EXAMINATION

No adequate summary of the *x*-ray data concerning sepiolite exists in the literature. Therefore it was necessary to compare the powder pattern of the Yavapai County material with a number of known sepiolite patterns. Most of these patterns were secured from the United States National Museum through the courtesy of Dr. Wm. F. Foshag. A partial list of the patterns used in the comparison follows:

Sepiolite—Chester County, Pennsylvania.
Sepiolite—Inyo County, California.
Sepiolite—Durango, Mexico.
Sepiolite—Dorsey Mine, Bears Creek Canyon, New Mexico.
Sepiolite—Bears Mountain, New Mexico.
Sepiolite—Little Cottonwood, Utah.
Sepiolite—Madagascar.

A routine comparison of these patterns with the pattern of the Yavapai mineral indicated their similarity. The position and intensity of each line was in close agreement. It was, however, necessary to calculate the interplanar spacings of each pattern so that an accurate comparison could be made.

The *x*-ray pattern of the Yavapai mineral was obtained by the powder method first using Mo K_α radiation but, subsequently, Cu K_α radiation was employed to obtain the high interplanar spacing values peculiar to sepiolite. The interplanar spacing values using Cu K_α radiation are given in Table 3.

TABLE 3. INTERPLANAR SPACINGS OF THE HYDROUS MAGNESIUM SILICATE, YAVAPAI COUNTY, ARIZONA

I	A.U.	I	A.U.	I	A.U.	I	A.U.	I	A.U.	I	A.U.
					Cu K_α						
S	12.3	M	3.75	M	2.61	W	2.05	W	1.55	W	1.31
W	7.52	W	3.53	S	2.55	W	1.95	W	1.51	W	1.29
W	6.75	M	3.35	M	2.44	W	1.86	W	1.49	W	1.27
W	5.02	M	3.18	W	2.38	W	1.72	W	1.46	W	1.25
W	4.51	W	3.04	M	2.25	W	1.69	W	1.43	W	1.00
S	4.29	W	2.82	W	2.18	W	1.66	W	1.40		
M	3.97	W	2.67	W	2.11	W	1.58	W	1.34		

Intensity: S, strong; M, medium; W, weak.

According to M. Urbain (1939) the line at 12.5 Å distinguishes sepiolite because it is definitely fibrous and not a phyllite. Kerr (1937, 1938) has shown that sepiolite is not related to the clay mineral montmorillonite as suggested by De Lapparent (1935, 1936). *X*-ray studies indicate a fibrous structure for sepiolite while montmorillonite and the high magnesia end member saponite have a fine micaceous habit suggesting a sheeted structure. It is thought by Longchambon (1936, 1937) that sepiolite is the main magnesium-bearing mineral of a group known as palygorskites. Other members of this group are altered amphiboles and the finely fibrous minerals asbestos, mountain leather and mountain cork.

M. Longchambon (1937) in describing fibrous sepiolite supports the distinguishing character of this high value by listing the first three lines of the pattern as 12.2 (±0.15) Å, 7.5 (±0.10) Å, and 6.7 (±0.05) Å.

The nature of the pattern of the Yavapai mineral indicates a high degree of crystallinity which is probably characteristic of the fibrous variety of this mineral.

TABLE 4. INTERPLANAR SPACINGS OF SEPIOLITE IN A.U.

(1)	(2)	(3)	(4)	(5)	(6
Mo K_α	Cu K_α	Mo K_α	Mo K_α	Mo K_α	Mo K_α
—	12.20	—	—	—	—
—	7.6	—	—	—	—
6.77	6.7	6.80	6.75	—	—
5.01	5.05	—	—	—	—
4.50	4.50	4.54	4.52	4.49	4.51
4.29	4.30	4.32	4.29	—	—
3.96	3.83	3.93	3.95	4.05	4.06
3.75	3.60	3.73	3.73	—	—
3.35	3.40	3.34	3.36	—	—
3.17	3.22	—	—	—	3.01
2.76	—	2.68	2.65	—	—
2.60	2.61	2.60	2.58	—	—
2.55	—	2.53	2.54	—	2.54
2.43	2.45	2.46	2.45	2.48	2.45
2.25	2.28	2.27	2.27	—	—
2.11	2.09	2.10	2.09	—	—
1.95	1.97	1.93	1.94	—	—
1.86	1.88	—	—	—	—
1.73	1.71	1.73	1.73	—	1.74
1.66	1.60	1.64	1.66	1.67	—
1.55	1.56	1.54	1.54	—	1.52
—	1.52	—	—	—	—
1.43	1.38	1.43	1.42	1.47	—
—	1.36	—	—	—	—
1.32	1.31	1.32	1.32	1.29	1.32
—	—	—	—	1.25	1.29
—	—	—	—	1.12	1.16
—	—	—	—	1.02	1.05

(1) Hydrous magnesium silicate from Yavapai Co., Arizona.
(2) Sepiolite, D'Ampandrandava; H. Longchambon (1937).
(3) Fibrous sepiolite, Madagascar; Mlle. Caillere (1933).
(4) Average of the United States National Museum specimens.
(5) Montmorillonite; P. F. Kerr (1937).
(6) Saponite; P. F. Kerr (1937).

Table 4 lists the interplanar spacings of the Yavapai mineral in comparison with those of Mlle. Caillere (1933), M. Longchambon (1937) and the average of the United States National Museum samples. The spacings for montmorillonite and saponite (Kerr 1937) are included to show the lack of agreement between the patterns of sepiolite and these two clay minerals.

SUMMARY

It has been the purpose of this paper to present chemical, optical, and *x*-ray data on a hydrous magnesium silicate from Yavapai County, Arizona, which is identified as fibrous sepiolite. The chemical composition as determined by a complete chemical analysis agrees satisfactorily with earlier published analyses for this mineral. The optical properties are in agreement, and the *x*-ray pattern compares favorably with those on record for sepiolite.

In addition to the original purpose, the evidence presented herein justifies the continued use of the term 'parasepiolite' rather than sepiolite when referring to the fibrous, highly crystalline variety of this mineral.

Schaller (1936) offers evidence that indicates there is only one type of sepiolite and its chemical formula is $2MgO \cdot 3SiO_2 \cdot 4H_2O$. There is, however, a variation in the refractive indices of sepiolite and in the number and development of the lines of the *x*-ray pattern. It seems logical to assume that these differences are due to physical rather than chemical conditions. The pattern of the Yavapai mineral consists of many well defined lines which indicate a high degree of crystallinity. This is supported by the lack of any 'amorphous' material as shown by studying fragments and thin sections. Sepiolite has been described, optically, by Michel (1913, 1914) and others as a mixture of a finely fibrous material and an 'amorphous' substance, probably of the same chemical composition. A specimen of sepiolite from Spain with a mean refractive index of 1.531 exhibits a poorly crystallized structure both under the microscope and in its *x*-ray pattern.

The refractive indices and the *x*-ray patterns are influenced by the degree of crystallinity. It seems that well crystallized specimens of sepiolite, free from impurities, have lower indices of refraction and well defined *x*-ray patterns, while an increase in the amount of the 'amorphous' material causes the refractive indices to be higher and the *x*-ray patterns less defined. The continued use of the term 'parasepiolite' for the well crystallized form of this hydrous magnesium silicate is therefore suggested.

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MINERALOGY OF THE OXIDES AND CARBONATES OF BISMUTH

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Abstract

The results of a survey of the mineralogy of the natural oxides and carbonates of bismuth are described. Bismutite, supposedly a hydrate, contains only non-essential water and has the composition Bi_2CO_5. On heating, bismutite and artificial $Bi_2CO_5 \cdot nH_2O$ lose water gradually to *ca.* 290°C. where the CO_2 is lost and $\alpha - Bi_2O_3$ remains. Artificial hydrates of Bi_2CO_5 are not known. Forty-six proven localities for bismutite are cited. Bismutosphaerite and basobismutite are identical with bismutite (which name has priority). Hydrobismutite and normannite are almost certainly identical with bismutite. Waltherite, a carbonate of bismuth of unknown formula, is a distinct species. Monoclinic, with $(110) \wedge (1\bar{1}0) = 116°34' \pm 20'$; $c_0 = 5.42 \pm 0.05$ Å. The crystals are zoned; mostly optically negative with 2V about 75° and dispersion $r < v$; $Y = b = 1.91 \pm$ and $X \wedge c = 16°$. The name beyerite is given to a new bismuth carbonate of unknown formula. Found at Schneeberg, Saxony, and Pala, San Diego Co., California. Beyerite is primitive tetragonal, with $a_0 = 3.78 \pm 0.01$, $c_0 = 21.77 \pm 0.05$; $a_0 : c_0 = 1 : 5.759$. Color yellow (crystals) to white or grayish-green (massive). The crystals are tiny thin plates, tabular (001) and beveled by (111). Optically negative, $\omega = 2.13 \pm 0.02$, $\epsilon = 1.99 \pm 0.02$.

It is proposed to restrict the name bismite to the alpha polymorph of Bi_2O_3, and the first proven natural occurrence of this material is described. The new name sillenite is given to a body-centered isometric polymorph of Bi_2O_3 found as a secondary product at Durango, Mexico. Fine granular; color, green and olive drab to yellowish; isotropic; the index of refraction is above 2.42; $a_0 = 10.08$. The evidence for the existence of a definite hydrate of bismuth oxide in nature is reviewed, and a probable natural occurrence of $Bi_2O_3 \cdot 3H_2O$ is described.

X-ray powder spacing data are tabulated for bismite, bismutite, sillenite, beyerite and waltherite.

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* Contribution from the Department of Mineralogy and Petrography, Harvard University, No. 261.

Introduction

The mineralogy of the oxygenated secondary compounds of bismuth, especially the oxides, carbonates, and arsenates, has been a standing problem, largely by virtue of the earthy and often admixed character of the material. The primary concern of the present study has been the identity of the natural oxides and carbonates of bismuth. It became necessary during the course of the work, however, to re-examine almost all of the secondary bismuth minerals. Some of the findings of the latter survey appear in this issue of the Journal.[1]

The writer wishes to express his appreciation to a number of persons who were of aid. Professor Harry Berman of Harvard University gave valued assistance throughout the investigation. Dr. E. S. Rittner of the Massachusetts Institute of Technology kindly presented samples prepared by him of the four known polymorphs of bismuth trioxide. Dr. W. F. Foshag and Mr. E. P. Henderson made available much material from the Roebling and other collections of the U. S. National Museum. Professor Paul F. Kerr of Columbia University and Dr. Fred H. Pough of the American Museum of Natural History loaned specimens from the mineral collections under their care. Type analyzed material and other specimens were obtained from the Brush collection of Yale University through the courtesy of Dr. George Switzer. Further study material was available from the collections of Harvard University and other sources. The *x*-ray spacing data were kindly calculated by Miss Betty Rogers. The spectrographic analyses were made through the courtesy of Mr. J. C. Rabbitt. Due to existing circumstances it seemed advisable to publish the paper even though several projected chemical analyses are not available.

Bismite

The supposed bismuth oxide, described by Wallerius in 1753, probably was a carbonate. The material analyzed by Lampadius in 1801 and accepted by some as an oxide, definitely appears to have been a carbonate (see Table 1, Column 1). The first real evidence of the occurrence of a bismuth oxide in nature was afforded by an analysis of Suckow in 1848 (Column 2). Later, a complete analysis was reported by Carnot (1874) on material from Meymac, France (Column 3), and analyses of very impure material from Tazna, Bolivia, apparently consisting for the most part of Bi_2O_3, were reported by Stelzner (1897). A number of additional occurrences have been mentioned but, with one exception, none of these are definitely proven. The orthorhombic morphology attributed to the mineral in Dana's *System* and Hintze's *Handbuch*[2] is based on measurements of artificial crystals of Bi_2O_3 by Nordenskiöld (1860).

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[1] Frondel, C., New data on agricolite, bismoclite, koechlinite and the bismuth arsenates: *Am. Mineral.*, **28**, 536–540 (1943).

Table 1. Analyses of Natural Bi_2O_3 (?)

	Bi_2O_3	As_2O_3	Sb_2O_3	Fe_2O_3	CO_2	H_2O	Rem.	Total
1.	86.3			5.2	4.1	3.4		99.0
2.	96.5	1.5		2.0				100.0
3.	96.7	0.13	0.22		0.68	0.95	1.06	99.74

1. Lampadius (1801). 2. Suckow (1848). Ullersreuth, Germany. 3. Carnot (1874). Meymac, France. Rem. is PbO 0.55, FeO 0.16, SO_3 0.15, HCl 0.20. S.G.=9.22.

Artificial Bi_2O_3 is known through the work of Sillén (1938, 1941) and of Rittner (1942) to exist in four polymorphous modifications: (1) A monoclinic, low-temperature form, α-Bi_2O_3, which corresponds to the supposed orthorhombic artificial crystals measured by Nordenskiöld. (2) A body-centered cubic form with $a_0=10.08$, which apparently requires for its existence a definite impurity content of Si, Al or Fe. (3) A simple-cubic form with $a_0=5.525$, and (4) a tetragonal phase with $a_0=10.93$, $c_0=5.62$ and space group $C\bar{4}2b$. Only one of the previously suspected natural occurrences of Bi_2O_3 can be identified as a particular polymorph. This material comprises microscopic crystals described by Rogers (1910) from Rincon, San Diego Co., California, which appear from his data to be α-Bi_2O_3.

In furtherance of this problem the writer examined 26 specimens from 15 localities, labelled bismite, available from various collections. Unfortunately, none of these proved to consist of Bi_2O_3; most were Bi_2CO_5 and the remainder were identified variously as bismuth arsenates and other materials. Later, an authentic natural occurrence of Bi_2O_3 came to hand among a small suite of bismuth minerals from Bolivia. This specimen, from the neighborhood of Colavi, consisted of a large water-worn cobble of native bismuth which was thickly incrusted by a coherent, fine-grained, grayish-green alteration product. The latter substance proved on x-ray powder study to be α-Bi_2O_3. Confirmatory chemical tests also were made. The x-ray spacing data are given in Table 2 and the pattern is shown in Fig. 1. Optically, the mineral is biaxial with high dispersion and indices above 2.42. Hardness$=4\frac{1}{2}$. The specific gravity, determined on the microbalance on a coarse powder, is 8.64.

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[2] See Hintze, C., *Handbuch der Mineralogie*, Leipzig, **1**, [2A], 1246 (1915).

Table 2. *X*-ray Powder Spacing Data for Bismite, Sillenite, Bismutite, Beyerite and Waltherite

Copper radiation; filtered

Bismite		Sillenite		Bismutite		Beyerite		Waltherite	
I	*d*	*I*	*d*	*I*	*d*	*I*	*d*	*I*	*d*
10	3.232	1	4.195	7	6.903	1	5.431	1	5.892
1	2.746	1	3.744	7	3.708	1	3.708	2	5.670
9	2.676	2	3.600	3	3.402	6	3.632	1	5.412
2	2.537	10	3.216	10	2.943	6	3.354	1	5.100
2	2.423	1	3.035	8	2.724	10	2.851	1	4.901
1	2.247	7	2.939	1	2.527	9	2.721	0.5	4.094
1	2.166	8	2.730	4	2.276	2	2.636	1	3.951
1	2.121	1	2.544	1	2.225	1	2.598	2	3.442
1	2.043	2	2.410	8	2.134	1	2.403	2	3.359
7.5	1.951	2	2.274	7	1.936	5	2.178	7	3.240
3	1.909	3	2.171	2	1.857	5	2.148	10	3.108
3	1.873	1	2.140	9	1.745	5	1.913	8	3.035
1	1.760	1	2.099	4	1.715	4	1.892	8	2.722
7.5	1.740	1	2.077	3	1.681	1	1.865	2	2.590
5	1.722	2	2.022	9	1.616	8	1.755	2	2.490
8	1.670	3	1.997	5	1.473	7	1.688	7	2.410
8	1.640	2	1.928	6	1.413	2	1.594	1	2.317
1	1.572	2	1.859	5	1.366	6	1.575	1	2.236
5	1.557	1	1.766	1	1.336	2	1.551	7	2.184
4	1.499	9	1.743	5	1.284	8	1.530	3	2.119
3	1.482	4	1.695	1	1.268	1	1.483	3	2.060
3	1.457	6	1.651	4	1.237	2	1.428	6	2.005
1	1.433	4	1.618	6	1.222	5	1.359	1	1.976
3	1.406	1	1.574	1	1.202	1	1.340	4	1.930
1	1.390	1	1.536	3	1.172	1	1.326	5	1.897
1	1.377	6	1.499	3	1.148	4	1.286	5	1.854
2	1.361	1	1.471	5	1.140	1	1.255	5	1.804
6	1.342	2	1.440	3	1.116	1	1.242	6	1.769
2	1.325	1	1.413	6	1.077	5	1.211	1	1.722
6	1.315	2	1.384	1	1.069	1	1.198	7	1.693
1	1.302	1	1.360	1	1.052	4	1.188	1	1.661
1	1.286	2	1.293	5	1.044	2	1.137	1	1.642
4	1.271	1	1.269	2	1.016	5	1.102	1	1.630
1	1.263	1	1.253	5	0.982	3	1.094	1	1.602
3	1.231	5	1.216	2	0.967	1	1.063	1	1.559
1	1.213	5	1.198	1	0.940	3	1.047	3	1.525
3	1.204	5	1.182	4	0.918	1	1.038	3	1.500
2	1.191	2	1.152	3	0.911	4	1.017	6	1.473
7	1.167	2	1.123	3	0.898	1	1.006	1	1.438
1	1.157	2	1.111	1	0.889	4	0.998	1	1.395
1	1.149	2	1.098	4	0.876	1	0.951	5	1.367
1	1.135	3	1.072	3	0.864	1	0.948	1	1.348
7	1.121	1	1.051	4	0.846	2	0.925	5	1.329
4	1.110	5	1.028	2	0.838	2	0.916	4	1.302
3	1.104	1	1.016	2	0.834	1	0.908	1	1.229
3	1.088	1	1.008			5	0.896	1	1.171
2	1.081	1	0.998			1	0.887	1	1.161
1	1.074	1	0.988			4	0.882	1	1.123
4	1.069	1	0.980			1	0.874	1	1.109
4	1.055	2	0.969			2	0.856	1	1.069
3	1.036	1	0.954			3	0.848	1	1.061

Note: With the exception of bismutite, spacings smaller than the last value given have been omitted from the Table.

Luster sub-resinous to sub-adamantine. Color grayish-green, with a grayish streak; artificial α-Bi_2O_3 is bright yellow in color. According to Sillén (1941) artificial α-Bi_2O_3 is monoclinic, pseudo-orthorhombic, with $a_0=5.83$, $b_0=8.14$, $c_0=7.48$; $\beta=67°4'$; contains Bi_8O_{12} in the unit cell; space group $P2_1/c$. The name bismite, originally proposed by J. D. Dana in the 5th (1868) edition of the *System*, may be restricted to α-Bi_2O_3. An isometric modification of Bi_2O_3 also occurs in nature and is described beyond as a new species, sillenite.

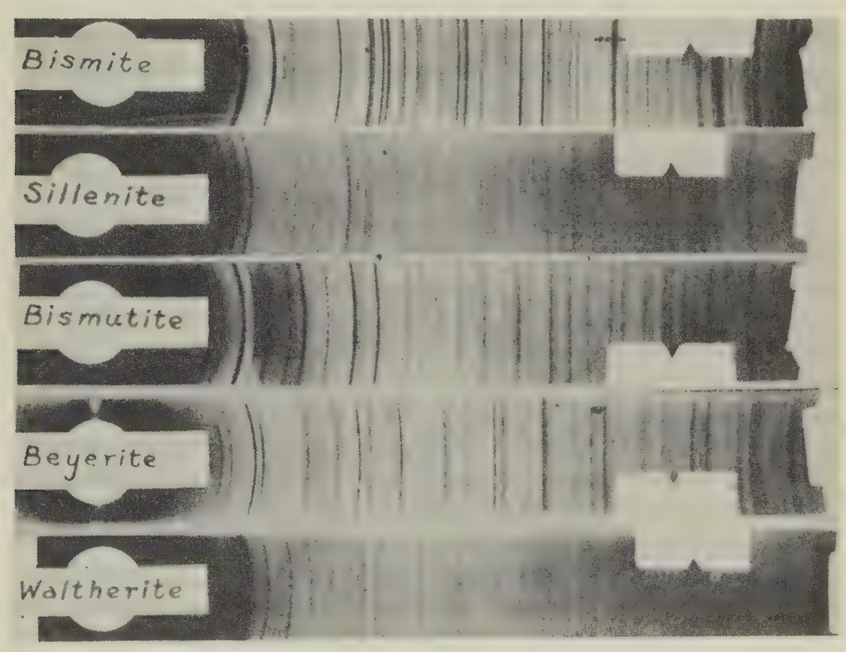

FIG. 1. *X*-ray powder patterns of bismite, sillenite, bismutite, beyerite and waltherite. Cu radiation.

SILLENITE (New Species)

The body-centered cubic modification of Bi_2O_3, described by Sillén (1938), was identified in specimens from Durango, Mexico. The mineral occurs as fine-grained granular masses intimately admixed with bismutite. In part the mineral forms waxy masses which closely resemble the bismutite itself. The color is olive-drab to olive-green, gray-green and green; also yellowish-green and yellow. Isotropic. The index of refraction is above 2.42. The color in transmitted light is a rich golden-brown to yellow in thick grains. Sufficient material was hand-picked for *x*-ray powder study and for spectrographic examinations. The spectrograph revealed only Bi in large amount together with traces of Si, Al, Cu, Fe, Ca and other elements. Excellent powder photographs were obtained which corresponded in every respect to the powder data of Sillén and to the pattern of a sample of artificial body-centered Bi_2O_3 prepared by Dr. E. S. Rittner. The x-ray powder spacing data are given in Table 2. Artificial body-centered Bi_2O_3 has $a_0 = 10.08$. The structure has been analyzed by Sillén (1938), who also discusses the rôle played by small amounts of Al and Fe present in artificial material. The calculated specific gravity for the cell contents $Bi_{24}O_{36}$ is 8.80. The name sillenite is proposed for the species after Dr. Lars Gunnar Sillén of Stockholm, who has contributed much to the knowledge of the polymorphs of Bi_2O_3.

BISMUTH HYDROXIDE

A number of artificial hydrates of Bi_2O_3 have been reported, but the dehydration and x-ray study of Hüttig, Tsuji and Steiner (1931) of the system H_2O-Bi_2O_3 indicates that only the compound $Bi_2O_3 \cdot 3H_2O = Bi(OH)_3$ exists. Their data, however, suggest that their compound is not the trihydrate but a dihydrate, and this view is accepted by Weiser (1935). No evidence was found by Hüttig, et al., or by Carfield and Woodward (1924) of the existence of $Bi_2O_3 \cdot H_2O = BiO(OH)$. This compound might be the end member of the isomorphous series between bismoclite, BiOCl, and daubreeite, BiO(OH,Cl).

The existence in nature of a bismuth hydroxide, or hydrated oxide, was first indicated by the work of Schaller (1911) on the bismuth ochers from San Diego Co., California. An analysis by Schaller of material from the Stewart mine conforms fairly well with the formula $Bi_2O_3 \cdot 3H_2O$, after the deduction of 26 per cent of hydrous impurities. Nevertheless doubt must be attached to this evidence because of the extremely small size of the analyzed sample (95 mg.), and of the uncertain assumptions made as to the nature of the impurities. An x-ray and dehydration study of this substance would be desirable, but no further material can be had. The occurrence in nature of a bismuth hydroxide also has been mentioned by Nenadkevich (1917) and Mountain (1935) but details are lacking.

In the course of the present work, a further occurrence of a substance possibly identical with $Bi_2O_3 \cdot 3H_2O$ was noticed. This material comprised creamy-white to yellow-layered, earthy crusts formed by the alteration of bismite (α-Bi_2O_3) from Colavi, Bolivia. Chemical tests indicated the substance to contain only Bi_2O_3 and H_2O. A water determination gave 9.2 per cent H_2O, which compares to the 10.4 per cent H_2O contained in $Bi_2O_3 \cdot 3H_2O$. However, no evidence is available to indicate whether the water is essential or not. The dehydrated material gave the x-ray pattern of α-Bi_2O_3. The fresh material gave an extremely faint and diffuse pattern which differed from those of the four polymorphs of Bi_2O_3. The pattern could not be identified with the x-ray pattern of the compound $Bi_2O_3 \cdot 3H_2O$, as represented by Hüttig, Tsuji and Steiner (1931). The x-ray data of these authors are given in such form, however, as to preclude any exact comparison. Artificial $Bi_2O_3 \cdot 3H_2O$ was prepared according to the procedure described by Hüttig, et al., but unfortunately this preparation did not give an x-ray pattern. Efforts to develop a pattern from both the natural and the artificial substances by heating resulted only in the gradual appearance of the pattern of α-Bi_2O_3. Optically, the natural material was very fine grained, seemingly isotropic, and of high index. The present data is not sufficient to establish the substance as a definite species.

Bismutosphaerite

Bismutosphaerite was first formally described and named by Weisbach in 1877. The mineral occurred as fibrous crusts with a spheroidal surface (to which the name alludes) at Neustädtel, near Schneeberg, Saxony. The same mineral had earlier been recognized by Beyer in 1805 and by Breithaupt in 1817. Weisbach examined the original specimens kept in Werner's collection. The analysis cited by Weisbach in the original description and later analyses[3] of material referred to this species all conform closely to the formula Bi_2CO_5. The original analyzed specimens of the material from Mexico, analyzed by Winkler (cited by Weisbach (1882)), and of material from Willimantic and Portland, Connecticut, analyzed by Wells (1887), were available for examination, together with seven non-type specimens of the fibrous, spheroidal mineral from Schneeberg. X-ray powder diffraction study proved the identity of this material with analyzed artificial Bi_2CO_5 and with bismutite. It is shown beyond that the mineral bismutite, which has been thought to be a definite hydrate, actually contains only non-essential water and is identical in all respects with artificial anhydrous Bi_2CO_5, and with bismutosphaerite. The name bismutite, proposed by Breithaupt in 1841, has priority.

Bismutite

The name bismutite was given by Breithaupt in 1841 to a bismuth mineral from Ullersreuth, Voightland, Germany. Qualitative chemical and blowpipe tests by Plattner, cited in the original description, indicated that the substance was a carbonate of bismuth containing small amounts of iron and copper as impurities, together with an extremely small amount of water. The water was ascribed by Breithaupt to admixed hydrous impurities. Schneeberg, Johanngeorgenstadt, and Aue, in Saxony, were cited as additional localities. The later usage of the name has been very indefinite in lack of characterizing crystallographic, chemical and physical data. In practice, the name appears to have been applied arbitrarily to bismuth carbonates that contained an apparently significant amount of water. Material with little or no water has been ascribed to bismutosphaerite. The conception that bismutite is hydrated dates from the first quantitative analysis, made by Rammelsberg (1849) on material from North Carolina, but this definitely is not the sense of the original description. The available analyses[4] are loosely grouped about the ratio $Bi_2O_3:CO_2=1:1$. Ordinarily from 1 to 3.5 per cent of water is present. A few analyses correspond to the formula $Bi_2CO_5 \cdot H_2O$, which requires 3.31 weight per cent H_2O, but this must be regarded in light of the findings to be described below, to be due only to chance. Many of the analyses were made on impure material.

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[3] Listed by Hintze, C., *Handbuch der Mineralogie*, Leipzig, **1**, [3A], 3403 (1929).

Material from 46 different localities, comprising about 70 specimens variously labeled bismutite or bismuth ocher, were available for examination. Several specimens from analyzed localities were represented. Suites of secondary bismuth ores from deposits near Hillside, Arizona, and near Tularosa, New Mexico, also were studied. These specimens without exception gave an x-ray powder diffraction pattern which was completely identical with that of artificial Bi_2CO_5 and of bismutosphaerite (Bi_2CO_5). The original specimens of Breithaupt's bismutite were not available, but three of the four original localities were represented. Dehydration data for two artificial preparations of $Bi_2CO_5 \cdot nH_2O$ and for two natural bismutites are given in Fig. 2. The water is lost continuously up to about 290°C., where the CO_2 is lost abruptly and α-Bi_2O_3 remains.[5] The available evidence indicates that bismutite has the composition Bi_2CO_5, and is not a hydrate but contains only non-essential water. The relatively large content of adsorbed and capillary water is not surprising in view of the fine-grained, earthy, or gel-like character and often metacolloidal origin of the mineral. A list of the localities for bismutite, proven by x-ray study, is given in Table 3. The x-ray powder data are given in Table 2 and Fig. 1. Bismutite is the only common carbonate of bismuth. The others—beyerite, boksputite and waltherite—are extremely rare.

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[4] Listed by Hintze, C., *Handbuch der Mineralogie*, Leipzig, **1**, [3A], 3406 (1929).

[5] The ignition product in these and similar experiments was identified by its x-ray pattern as α-Bi_2O_3, but the writer has been informed by Dr. E. S. Rittner that the tetragonal modification of Bi_2O_3 sometimes is formed.

Table 3. Proven Localities for Bismutite

United States

Anderson Apache mine, Hachita, New Mexico.
Casher's Valley, Jackson Co., North Carolina.
Gaston Co., North Carolina.
The Granites, near Bagdad copper mine, 30 miles west of Hillside, Yavapai Co., Arizona. Mostly pseudomorphous after bismuthinite.
Salida, Chaffee Co., Colorado.
Las Animas, La Plata Co. (?), Colorado. After bismuthinite.
Telluride, San Miguel Co., Colorado.
Maricopa Co., Arizona.
Lillian mine, Leadville, Colorado. Alteration of bismuth sulfosalts.
Petaca, New Mexico. In pegmatite.
Mohave Co., Arizona.
Eagle Station, Sierra Co., New Mexico.
Grand View claim, San Andreas Mtns., west of Tularosa, New Mexico.
Pioneer claim, San Andreas Mtns., New Mexico.
30 miles west of Tularosa, New Mexico.
Mammoth mine, Tintic, Utah.
Hales Quarry, Portland, Connecticut. In pegmatite after bismuthinite.
Willimantic, Connecticut.

South America and Mexico

El Casse, Durango, Mexico. Alteration of native bismuth.
El Carmen mine, Durango, Mexico. In part after native bismuth.
Unspecified locality in Durango, Mexico.
Guanajuato, Mexico. After an unidentified tetragonal mineral.
San Luis Potosi, Mexico.
Sao Jose de Bryamba, Minas Geraes, Brazil.
Itabira de Matto Grosso, Brazil. After bismuthinite.
Huarancaca, Peru.
Pueblo Viejo, Esmoraca, Bolivia. After bismuthinite.
Carmen mine, Huanya, Potosi, Bolivia. After native bismuth.
Santa Vela Cruz, near Pongo, Bolivia.
San Baldomero mine, Sorata, Bolivia. After bismuthinite.
Tazna, Bolivia. Specimens from several different places in this district; mostly an alteration of bismuthinite.
Isca-Isca, Bolivia. Alteration of native bismuth.
La Reforma, Chorolque, Bolivia. Alteration of bismuthinite.
Espiritu Santo, Chorolque, Bolivia. After bismuthinite.

Other Localities

Kingsgate, New South Wales.
Ukalunda, Queensland.
Schorl Mtn., Transbaikalia, Russia. After bismuthinite(?)
Beresov, Urals, Russia. After aikinite (?)
Ampangabe, Madagascar.
Meymac, France.

Restormel mine, Cornwall, England. Another specimen from an unspecified locality in Cornwall.
Tavistock, Devonshire, England.
Aue, Saxony. After bismuthinite.
Joachimsthal, Bohemia.
Ullersreuth, Voightland, Germany. After bismuthinite.
Schneeberg, Saxony. A suite of 11 specimens from various mines in this district.

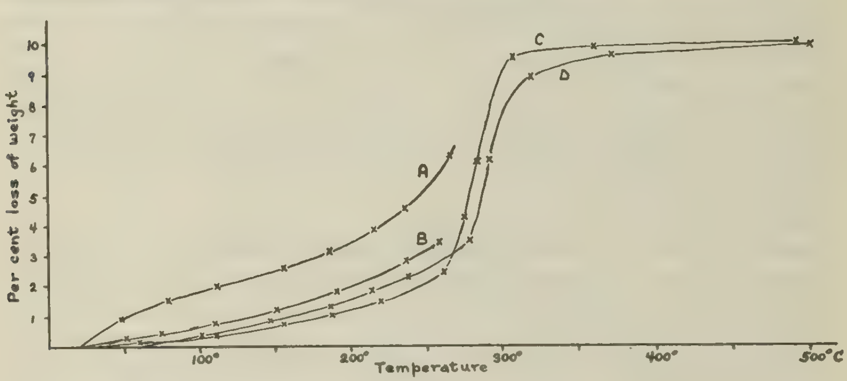

FIG. 2. Dehydration data for $Bi_2CO_5 \cdot nH_2O$. A. Artificial $Bi_2CO_5 \cdot nH_2O$. Precipitated by conc. ammonium carbonate at 13°C. Air dried at room temperature. B. Natural bismutite. Semivitreous material from Eagle Station, New Mexico. Contains 3.8 per cent H_2O. C. Artificial "$Bi_2CO_5 \cdot H_2O$" of Lefort (1848). Air dried at room temperature. D. Natural bismutite. Earthy, straw colored. Tazna, Bolivia. All determinations made by heating to constant weight.

Physical Properties of Bismutite. Distinct crystals of bismutite have not been found. The mineral occurs as pulverulent to dense and hard earthy masses, as opaline crusts, and as radially fibrous crusts or spheroidal aggregates; rarely as lamellar, pearly, aggregates. Bismutite often possesses a prismatic or other pseudomorphous structure. The hardness ranges up to 3½ in material tested by the writer, but values up to 5½ have been cited. The specific gravity is quite variable. The values given in the literature range for the most part between 6.8 and 7.67. The writer obtained the following values for the specific gravity, using a microbalance:

6.61 (Meymac, France)
6.74 (San Andreas Mtns., N. M.)
6.77 (Hillside, N. M.)
6.95 (Petaca, N. M.)
7.24 (Willimantic, Conn.)
7.33 (Mohave Co., Arizona)

The color of the mineral is variously straw- to brownish-yellow and citron-yellow (the most common colors), brown, green, white, greenish-gray, gray; rarely bluish-green or blue. The blue tint was found in several instances to be caused by included malachite, and in one instance to mixite. Sometimes deep gray to black in color, especially in the interior portions of pseudomorphs after bismuthinite. Under the microscope, bismutite ordinarily appears as indistinctly polarizing cryptocrystalline grains. The mean index is quite variable and ranges from below 2.12 to above 2.30. The birefringence appears to be moderately large and is estimated by Larsen (1921) at about 0.05. Fibrous material usually has parallel extinction and positive elongation. There appears to be a good cleavage, with an optic axis perpendicular thereto.

Artificial Hydrous Bismuth Carbonate. Two artificial carbonates of bismuth have been reported: the anhydrous compound Bi_2CO_5, and a hydrate $Bi_2CO_5 \cdot H_2O$. The synthesis of the latter compound, reported by Lefort (1848), was duplicated and the substance was found on *x*-ray and dehydration study (Fig. 2) to be only Bi_2CO_5 with adsorbed and capillary water. The precipitates obtained by adding solutions of alkali, or ammonium carbonates, or of alkali bicarbonates to bismuth nitrate solutions, together with commercial, C.P., preparations of bismuth sub-carbonate or basic-carbonate, all proved on *x*-ray study to be identical with anhydrous Bi_2CO_5. The air-dried precipitates ordinarily contain up to several per cent of loosely held water. The freshly prepared carbonate often gives a rather diffuse and faint *x*-ray pattern, which becomes sharp after ageing in the mother-liquid, or after slight heating. The particle size and water content of the material is noticeably influenced by the concentration of the reagents and especially by the temperature. The dehydration curve of an air-dried sample of a highly voluminous and hydrous precipitate obtained with ammonium carbonate at 13° is shown in Fig. 2.

HYDROBISMUTITE

This name was given by Nenadkevich (1917) to a supposed hydrated bismuth carbonate, $Bi_2CO_5 \cdot 2\text{–}3H_2O$, from Transbaikalia, Russia. Specimens were not available for study. The material was thought to differ from bismutite in containing more water. It is practically certain that this substance is merely bismutite containing a relatively large amount of non-essential water.

BASOBISMUTITE

The above name was given by Nenadkevich (1917) to a supposed hydrated bismuth carbonate, $Bi_4CO_8 \cdot H_2O$, found as gray, earthy masses on Schorl Mtn., Transbaikalia, Russia. Analysis gave: Bi_2O_3 94.49, CO_2 4.07, H_2O 1.43, Cl 0.12; total 100.11. A type specimen obtained by the U. S. National Museum by exchange was available for study. *X*-ray study proved the mineral to be identical with bismutite. Optically, the material was very fine-grained and impure.

NORMANNITE

A name that was given in a manuscript by Weisbach in 1877 to an ill-characterized brownish bismuth carbonate, supposedly Bi_6CO_{11}, found in spheroidal aggregates at Neustädtel, near Schneeberg, Saxony (see Tetzner and Edelmann (1926)). It seems likely that this material is identical with that from the same locality described under the name bismutite by Weisbach in 1880, inasmuch as the analysis there cited yields the formula $Bi_6CO_{11} \cdot H_2O$. In any case, this substance, as remarked by Schairer (1930), presumably is identical with Bi_2CO_5, bismutite.

BOKSPUTITE

The name boksputite was given by Mountain (1935) to a carbonate of lead and bismuth, $Bi_2Pb_6C_3O_{15}$, from Boksput, in Gordonia, Cape Province, South Africa. The mineral occurs as fine-grained, yellow masses. Hardness $3\frac{1}{2}$; specific gravity 7.29. The material has a slightly pearly luster apparently due to a cleavage or a scaly habit. *X*-ray powder photographs are stated to be distinctive, but no spacing data are given. Specimens of this apparently distinct species could not be obtained for examination. Genth (1892) cited analyses of a bismuth carbonate from Colorado which show 4.6-5.0 per cent PbO, but the lead clearly appears to be due to admixture.

BEYERITE (New Species)

The new species here described was first found as pulverulent earthy masses and drusy crystals on specimens from Schneeberg, Saxony, and was later recognized in massive earthy form on a specimen from Pala, San Diego Co., California. The material from Schneeberg comprised sparkling rectangular plates up to 0.5 mm. in size scattered over chalcedonic quartz and bismutite. The tetragonal crystals are extremely thin plates flattened on (001), and are commonly grouped into subparallel aggregates or rosettes. The plates are bounded laterally by two equivalent line faces from which accurate measurements could not be obtained. The measured ρ values varied between 81°55′ and 79°25′ with an average value of 81°32′; this value corresponds to the value 81°17′ for (111) in the *x*-ray structural cell. A crystal drawing is shown in Fig. 3. The mineral ordinarily is in the form of distinct crystals, but sometimes forms soft, white, microcrystalline masses. One specimen exhibited compact earthy pseudomorphs of yellow beyerite after embedded cubic crystals of smaltite (?). Entirely satisfactory Weissenberg and rotation *x*-ray data could not be obtained due to the markedly imperfect character of the crystals. Approximate cell dimensions were obtained from rotation films taken about [001], [100] and [101], and these were refined by Weissenberg 0-layer measurements, as follows:

$$a_0 = 3.78 \pm 0.01 \qquad c_0 = 21.77 \pm 0.05; \qquad a_0 : c_0 = 1 : 5.759$$

The following data also were obtained: symmetry, tetragonal centrosymmetrical, D_{4h}; space lattice type, primitive; $00l$ present only when $l = 2n$. Cu radiation was employed.

The observed specific gravity, measured by the microbalance on massive material from California, is 6.56. The x-ray powder spacing data are given in Table 2 and the pattern shown in Fig. 1. No cleavage was observed. The hardness is 3 or less. Color, bright yellow to lemon-yellow (crystals) and, in massive material, yellowish-white to white (Schneeberg) or grayish-green to gray (California). Streak white. Luster vitreous. Optically, uniaxial negative (−). The indices were determined in phosphorus-methylene iodide and sulfur-selenium melts as: $\omega = 2.13 \pm 0.02$, $\epsilon = 1.99 \pm 0.02$. Some crystals have an anomalous biaxial character with very small 2V. Not pleochroic. The indices ($\omega = 2.13$, $\epsilon = 1.94$) given by Larsen (1921) for platy yellow crystals labeled bismutosphaerite from Schneeberg, doubtless refer to this species. Beyerite occurs at the Stewart mine, Pala, California, as compact masses of a greenish-gray color embedded in massive quartz. Here the mineral appears to be an alteration product of a primary bismuth mineral in the pegmatite.

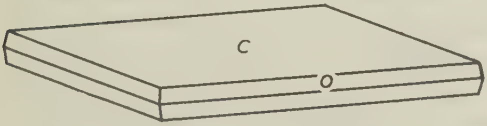

FIG. 3

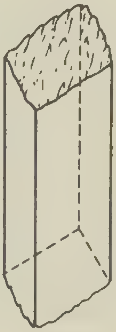

FIG. 4

A spectrographic examination of a small, handpicked sample of the crystals from Schneeberg revealed the presence of a large amount of Bi and a lesser amount of Ca together with traces of Si, Al, Mn, Pb, Mg, Cd and Cu. The mineral effervesces briskly in dilute HCl. An unnamed mineral from Schneeberg very briefly described by Arzruni and Thaddéeff in 1899 is almost certainly identical with beyerite. The mean of two partial analyses by Thaddéeff on very small samples, after deducting quartz 8.33 and Fe_2O_3 1.50 per cent, is Bi_2O_3 90.0, CaO 3.5, CO_2 4.6, H_2O 1.0; total 100.0. Beyerite appears to be a carbonate of bismuth and calcium, but a definite formula must await a new analysis. A possibly similar mineral from Argentina was analyzed by Bodenbender (1899).

The name beyerite is proposed for this well-defined new species after Adolph Beyer (1743–1805), a mining engineer and mineralogist of Schneeberg, Saxony, who in 1805 recognized the occurrence of a bismuth carbonate in nature. Beyer's mineral was later shown by Weisbach (1877) to be bismutite, Bi_2CO_5.

WALTHERITE

This little known mineral was briefly described in 1857 by Vogl as a bismuth carbonate found in thin prismatic crystals associated with torbernite, at Joachimsthal, Bohemia. The color was described as siskin-green to clove-brown, and the luster as vitreous. On the basis of a qualitative examination by Lindacker (cited by Vogl) the mineral was believed to contain Bi_2O_3, CO_2, H_2O, and silica. Later, Bertrand (1881) examined specimens of waltherite and recognized two apparently distinct minerals: (1) A brown mineral with a prism angle of 116° and cleavages parallel to $\{110\}$, $\{010\}$ and $\{001\}$. Optically positive, with $X=c$, $Y=b$ and $Z=a$. (2) A green mineral not as easily cleavable as the first, optically negative, with the acute bisectrix, instead of the obtuse bisectrix, perpendicular to the best cleavage.

Several non-type specimens labeled waltherite from Joachimsthal were available for study. These exhibited a few tiny, imperfect, crystals of a brownish prismatic mineral which reacted qualitatively for Bi and CO_2. The x-ray powder pattern and optical constants of this mineral are distinct from those of the other bismuth minerals, and there appears to be no question but that waltherite is a distinct species. The x-ray spacing data are given in Table 2 and the pattern shown in Fig. 1. The color of the mineral ranges from dark olive-drab to brownish-green, and often passes inwardly into a yellowish-green. The apical portions of some crystals are deep brown. The luster is sub-resinous to vitreous. Hardness about 4. The specific gravity was determined by means of the microbalance on 17 mg. of coarse powder as 5.32—a value which seems low in view of the composition of the mineral. The crystals are doubly terminated and are monoclinic in appearance, as shown in Fig. 4. The terminal form is too rough to measure and only an approximate value, $116° 34' \pm 20'$ could be obtained for the prism. An x-ray rotation photograph taken with Cu radiation gave the [001] period as 5.42 ± 0.05 Å. Crushed crystals yield both brown and green grains with rather unlike optical properties. The brownish material is biaxial negative with 2V about 75° and has strong birefringence. $Y=b=1.91\pm$ and $X \wedge c=16°$; dispersion $r<v$. Weakly pleochroic in brown with absorption $X=Y<Z$. Most of the greenish material has higher indices and stronger birefringence. A few grains had 2V up to 90° and others were optically positive with dispersion $r>v$. The x-ray powder patterns of the green and brown materials are identical.

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NEW DATA ON AGRICOLITE, BISMOCLITE, KOECHLINITE, AND THE BISMUTH ARSENATES

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ABSTRACT

Agricolite is identical with eulytite. Rhagite is identical with atelestite. Arsenobismite from Tintic, Utah, is a valid species and a new locality at Tazna, Bolivia, is noted. A new but un-named bismuth arsenate is briefly described and three localities are cited. Two new localities are cited for both koechlinite and bismoclite. *X*-ray powder spacing data are tabulated for atelestite, arsenobismite, koechlinite, and for a new un-named bismuth arsenate.

IDENTITY OF AGRICOLITE WITH EULYTITE

Eulytite, $Bi_4Si_3O_{12}$, occurs as well-developed isometric hextetrahedral crystals. The material usually is weakly birefringent, and has been thought to be only pseudo-isometric at ordinary conditions. Some crystals are internally divided into uniaxial segments, or show polysynthetic birefringent twinning lamellae. The optical anomalies have been described by Bertrand (1881). The *x*-ray powder diffraction effects, however, are completely accounted for on the basis of a hextetrahedral structure, as shown by Menzer (1931), and any departure from isometric symmetry must be slight. The calculated specific gravity, 6.82, is considerably greater than the observed values. The writer obtained 6.61 for yellow eulytite crystals and 6.63 for massive agricolite (=eulytite), using a microbalance. Menzer obtained 6 6±0.2 and Rath (1869) gave 6.106 for eulytite. Agricolite of Frenzel (1873) has been thought to be a monoclinic polymorph of eulytite. The supposed monoclinic character was based on very inconclusive evidence (see Groth cited by Frenzel (1873)). The writer examined several specimens of agricolite from both Schneeberg and Johanngeorgenstadt, Saxony. This material comprised radial, semi-globular aggregates and answered the original description in all details. The *x*-ray powder pattern proved to be completely identical with that of eulytite. Optically, agricolite is very weakly birefringent. The mean index of both agricolite and eulytite varies slightly in different specimens but for the most part is about 2.04. Eulytite as presently constituted and agricolite must be accepted as identical. The possibility exists that agricolite represents a primary occurrence of the inversion product (?) of a truly isometric eulytite. The name eulytite (eulytin), proposed by Breithaupt in 1827, has priority. The mineral from Schneeberg later named agricolite was known to Breithaupt in 1827 and was, in fact, considered by him to be identical with eulytite.

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* Contribution from the Department of Mineralogy and Petrography, Harvard University, No. 262.

Bismoclite

Bismoclite, BiOCl, was described in 1935 by Mountain from Namaqualand, South Africa. The crystal structure of BiOCl together with the identity of the natural and artificial materials was established by Bannister (1935). More recently, Schaller (1941) has shown that the so-called crystallized bismite from Goldfield, Nevada, is bismoclite. Two additional localities for bismoclite may be mentioned. The mineral was found as dense grayish-green masses in a greisen-like rock from Bygoo, New South Wales. Under the microscope the substance appeared as indistinct shreds and plates with an occasional semblance of a square outline. The bismoclite is an alteration product of embedded masses of some other bismuth mineral. Bismoclite also was identified as grayish-green, compact masses from Tintic, Utah. This material was microcrystalline and admixed with limonite, quartz and other impurities. Daubreeite, BiO(OH, Cl), a mineral shown recently by Bannister (1935) to be a member of an isomorphous series with bismoclite, was doubtfully reported by Means (1916) from Tintic, Utah. Mean's original specimens were available for study but the particular substance to which he was referring could not be identified. His mineral probably was bismoclite.

Koechlinite

This species was described by Schaller in 1916 as an orthorhombic bismuth molybdate, Bi_2MoO_6, from Schneeberg, Saxony. Part of the original material was available for study. The *x*-ray powder spacings are given in Table 1. The pattern is rather similar to that of tetragonal Bi_2O_3. Two new localities may be reported. The mineral occurs as small lamellar aggregates of a yellow color embedded in massive milky quartz at the Dunallan gold mine, Coolgardie, Western Australia. The material is an alteration product, probably of tetradymite. Between crossed nicols some of the flakes of the mineral have a mottled appearance due to a variation in birefringence and seem to be altered. The original koechlinite from Schneeberg shows similar features, as described by Schaller. Koechlinite also was found as soft white to yellow masses associated with bismoclite on specimens from Bygoo, New South Wales. Here, too, the mineral has formed by the alteration of a pre-existing bismuth mineral.

Bismuth Arsenates

Five different arsenates of bismuth have been reported from nature: walpurgite, mixite, atelestite, rhagite, and arsenobismite. Walpurgite and mixite appear to be valid species although our knowledge of them leaves much to be desired. A new occurrence of mixite can be mentioned. The mineral was found as thin, cross-fiber veinlets and needles in bismutite in specimens from Durango, Mexico.

Several non-type specimens of atelestite (Breithaupt, 1832) and of rhagite (Weisbach, 1874), both from the original locality at Schneeberg, Saxony, were available for study. The atelestite comprised adamantine sulfur-yellow crystals of characteristic habit. The rhagite formed yellowish-green mammillary crusts and otherwise answered the original description. The two minerals gave identical x-ray powder patterns. It proved impossible to measure the optical characters of rhagite, due to the finely fibrous nature of the mineral, but such data as could be obtained agreed with the properties of atelestite. The composition of the two minerals differs only in the ratios, which are based on quite unsatisfactory analyses. Rhagite may be accepted as identical with atelestite. The latter name has priority. The x-ray powder spacing data for atelestite are given in Table 1.

The original analyzed specimens of arsenobismite of Means (1916) from Tintic, Utah, were obtained through the courtesy of Prof. Walter H. Newhouse of the Massachusetts Institute of Technology. The qualitative composition of the mineral was verified by chemical tests. The x-ray pattern and optical characters are distinctive. Optically, arsenobismite is nearly or quite isotropic with an index of refraction above 1.86. The x-ray powder spacing data are given in Table 1. Arsenobismite must be considered as a valid species, but the formula is very uncertain. A second occurrence of arsenobismite was found as yellowish-brown ochreous masses from Tazna, Bolivia.

A new and distinct arsenate of bismuth occurs abundantly in association with arsenobismite at the Mammoth mine in the Tintic district, Utah. The mineral forms pulverulent masses of a dead-white color impregnating friable quartzose and limonitic gossan material. The mineral alters to arsenobismite. Under the microscope this mineral is extremely fine-grained with apparently a moderate birefringence and with indices above 2.04. It is attacked by sulfur-selenium melts and by phosphorus-methylene iodide liquids. The same mineral was found abundantly as pulverulent white to yellow masses in specimens from Tazna, Bolivia, and in one instance was outwardly altered to arsenobismite. A third occurrence was found as thin orange crusts on a specimen of pucherite from Schneeberg, Saxony. The x-ray powder spacing data for this new arsenate are given in Table 1. It is hoped to give a more complete description of this mineral and of arsenobismite at a later time. In connec-

Table 1. *X*-Ray Powder Spacing Data for Koechlinite, Atelestite, Arsenobismite and a New Un-named Bismuth Arsenate

Copper radiation; filtered

Koechlinite		Atelestite		Arsenobismite		New Arsenate	
I	*d*	*I*	*d*	*I*	*d*	*I*	*d*
10	3.131	2	6.798	9	6.056	1	8.488
6	2.733	2	6.098	6	3.715	1	6.226
5	2.683	6	4.221	2	3.341	2	4.545
1	2.588	10	3.234	10	3.108	1	4.191
3	2.473	7	3.115	6	3.001	10	3.280
1	2.419	2	2.939	5	2.860	9	3.200
2	2.263	7	2.720	5	2.570	9	3.108
6	1.936	5	2.522	1	2.392	4	3.026
8	1.918	2	2.305	6	2.276	2	2.866
1	1.879	6	2.200	2	2.113	1	2.825
1	1.769	5	2.121	7	1.997	2	2.717
9	1.647	6	2.033	8	1.843	4	2.621
7	1.628	5	1.973	1	1.774	1	2.591
6	1.570	5	1.885	2	1.717	3	2.500
2	1.524	1	1.831	2	1.690	1	2.392
1−	1.486	4	1.803	3	1.568	2	2.282
1−	1.423	2	1.733	3	1.546	3	2.223
1	1.397	4	1.685	3	1.507	1	2.191
3	1.369	6	1.641	1	1.430	2	2.128
3	1.346	3	1.575	1	1.416	3	2.073
1	1.323	3	1.548	1	1.393	8	1.983
4	1.257	4	1.511	2	1.350	5	1.913
6	1.246	2	1.468	1	1.290	2	1.874
5	1.223	2	1.447	2	1.253	2	1.842
4	1.209	4	1.416	1	1.225	5	1.804
1	1.151	1	1.373	1	1.191	2	1.754
5	1.116	4	1.290	1	1.156	2	1.722
4	1.107	1	1.264	1	1.123	5	1.682
4	1.053	1	1.229	1	1.056	1	1.654
3	1.039	3	1.201	1	0.995	1	1.632
1	1.008	1	1.174	1	0.875	2	1.610
3	0.971	2	1.157	1	0.862	7	1.576
5	0.925	2	1.144			2	1.545
5	0.917	3	1.129			1	1.545
1	0.913	2	1.110			1	1.452
5	0.908	2	1.078			2	1.432
1	0.899	2	1.051			1	1.418
4	0.867	1	1.023			1	1.383
4	0.855	1	1.007			1	1.350
5	0.834	1	0.991			1	1.325
1	0.829	1	0.962			1	1.308
1	0.827	1	0.951			1	1.294
1	0.825	1	0.939			1	1.269
		1	0.925			1	1.246
		4	0.909			2	1.223
		2	0.896			2	1.095
		4	0.885				
		4	0.877				
		5	0.863				

tion with this work, the artificial compound $BiAsO_4$ was prepared by precipitating a weakly acid solution of bismuth nitrate with a slight excess of Na_2HAsO_4. The air dried precipitate and samples that had been heated three hours at 750°C. gave identical *x*-ray powder patterns which differed from those of all of the natural bismuth arsenates.

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NOTES AND NEWS

SOME NOTES ON THE CALCULATION OF MOLECULAR FORMULAE FOR GLAUCONITE

C. O. Harvey, *Geological Survey and Museum, London, S.W.7.*

Hendricks and Ross[1] propose for glauconite a formula of the general type $X_A(\mathrm{Al, Fe''', Fe'', etc.})_\Sigma(\mathrm{Al, Si})_4\mathrm{O}_{10}(\mathrm{OH, F})_2$, where X = (K, Ca, Na, etc.), A = 1.00 or less, and Σ must be 3 or less. They state that a convenient method for calculating a formula is to reduce the analytical values of the ions having octahedral and tetrahedral coordination to their molal values, and then to assume that Al is distributed between tetrahedral and octahedral coordination so as to have $\Sigma = 2.00$. Further calculation provides a figure (f) for (Al, Si), and the amounts of the various ions in the trial formula are now obtained by a calculation which includes multiplying their molal values by 4/f. They find that the sum of the cation valencies given by this trial formula will, in general, differ from the figure 22, required to balance the 10 oxygen atoms plus 2 hydroxyls, and, in order to bring the two figures into agreement, aluminium must be interchanged between tetrahedral and octahedral coordination. Hendricks and Ross do this by trial and error, and thus arrive at a formula for any particular specimen of glauconite.

Table 1

	%	Mols.	Metal +silicon atoms	Valencies	Metal+silicon atoms per 22 valencies	Formula	Hendrick & Ross Formula
SiO_2	49.4	0.8225	0.823	3.292	3.619	3.62 } *4.00*	3.63 Si
Al_2O_3	10.2	0.1001	0.200	0.600	0.879	0.38	0.37 Al
						0.50 } *2.06*	0.51 Al
Fe_2O_3	18.0	0.1127	0.225	0.675	0.990	0.99	0.99 Fe'''
FeO	3.1	0.0432	0.043	0.086	0.189	0.19	0.18 Fe''
MgO	3.5	0.0868	0.087	0.174	0.383	0.38	0.38 Mg
CaO	0.6	0.0107	0.011	0.022	0.048	0.05 } *0.73*	0.75 { Ca
K_2O	5.1	0.0541	0.108	0.108	0.475	0.48	K
Na_2O	1.4	0.0226	0.045	0.045	0.198	0.20	Na
Total				5.002			

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[1] *Am. Mineral.* **26** 683–708 (1941).

The main object of the present notes is to point out that this somewhat elaborate calculation is not necessary.

Hendricks and Ross initially make the assumption that the total number of metal plus silicon ions is 6, but they subsequently assume that the formula contains 10 oxygen atoms plus 2 hydroxyls (i.e. 22 valencies). As the latter assumption is to be made, one may just as well make it at the beginning of the calculation, and proceed on this basis.

Table 2

	%	Metal+silicon atoms per 22 valencies		
SiO_2	50.40	3.750	Si 3.750	*4.00*
Al_2O_3	6.46	0.566	Al 0.250	
			Al 0.316	*2.02*
TiO_2	0.09	0.005	Ti 0.005	
Fe_2O_3	20.17	1.128	Fe''' 1.128	
FeO	1.43	0.089	Fe'' 0.089	
MnO	0.02	0.001	Mn 0.001	
Cr_2O_3	0.03	0.002	Cr 0.002	
MgO	4.34	0.481	Mg 0.481	
Li_2O	tr.			
K_2O	7.57	0.718	K 0.718	*0.74*
Na_2O	0.11	0.016	Na 0.016	
Rb_2O**	0.02	0.001	Rb 0.001	
Cs_2O**	not found			
BaO**	not found			
H_2O above 105°C.	5.02	(H, 2.493)		
H_2O below 105°C.	4.06	(H, 2.013)		
CaO**	0.03			
P_2O_5	0.04			
CO_2	0.0			
S	0.03			
	99.82			
F	<0.02			

** Based on spectrographic work by J. A. C. McClelland.
Magnetic separation by A. F. Hallimond.
Analyst, C. O. Harvey.

By ignoring the analytical figures for H_2O and F, and calculating on the basis of 11 oxygen atoms, one may, by the usual procedure, calculate the proportions of the metal and silicon ions. Alternatively, one may work on a valency basis, assuming 22 valencies, as indicated in Table 1. The example is taken from the paper by Hendricks and Ross (p. 689), and the figures obtained by their method of calculation are quoted for comparative purposes.

A sample of glauconite was recently obtained by magnetic separation from the glauconite sand in the middle division of the Bracklesham Beds, Chobham Common, Surrey. The figures obtained by chemical analysis and the interpretation by the method outlined in Table 1 are given in Table 2.

This sample of glauconite contains very little Ca (only sufficient to combine with the P_2O_5), and only a small amount of Na, X being almost entirely potassium.

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PROCEEDINGS OF SOCIETIES

PHILADELPHIA MINERALOGICAL SOCIETY

The Academy of Natural Sciences of Philadelphia, March, 4, 1943

A meeting was held on the above date with Dr. W. Hersey Thomas presiding. Fifty-four members and visitors were present. Professor Richmond E. Myers of Muhlenberg College gave an illustrated talk on "Pennsylvania the Unsuspected." Points of geological and mineralogical interest were shown by slides, such as the Grand Canyon at Wellsboro, the cement district of the Lehigh region, the slate deposit at Slatington, the Kibblehouse quarry, and the Rock City conglomerate deposit at the northern border, which exhibits large open eroded veins. Views were shown of the jasper cliffs located in the hills above Reading which were extensively worked by the Indians for their arrowheads. Diggings and dumps still remain in which Indian relics are occasionally found. Professor Myers stated that recent borings at Friedensville indicate that zinc deposits still exist in the unworked areas and that possibly the region may be mined again.

Meeting of April 1, 1943

Dr. W. Hersey Thomas presided. Fifty members and visitors were present. Dr. Joseph L. Gillson addressed the Society on "The Flotation Process of Ore Concentration."

John Cochrane exhibited a specimen of the rare element indium and tubes containing small nuggets of native osmiridium.

Meeting of May 6, 1943

Forty-one members and visitors were present with Dr. W. Hersey Thomas presiding. Dr. Duncan Stewart, Jr., of Lehigh University gave a lecture on "The Petrography of Antarctic Rocks." Paul Seel reported on trips taken to Prospect Park, Kibblehouse quarry and Wheatley mine and exhibited a number of specimens.

Meeting of June 3, 1943

Dr. W. Hersey Thomas presided. Forty-one members and visitors were present. Dr. J. F. Schairer of the Geophysical Laboratory addressed the Society on "The Rock-forming Minerals and their Origin." Dr. Schairer explained the methods used in the laboratory for determining just what happens when a molten magma cools and solidifies slowly, and how the magma changes its composition during this crystallization process. The common minerals of the igneous rocks were dealt with in turn, namely, the olivines, pyroxenes, amphiboles and micas, feldspars, and finally quartz.

The relationship between the olivine series and the pyroxenes was mentioned. A number of melting point curves were shown and explained. Slides were shown illustrating some of the equipment that is used in carrying out this type of investigation.

J. S. Frankenfield, *Secretary*

NEW MINERAL NAMES

Hanušite

Jan V. Kašpar: Hanušite, a new mineral. *Chem. Listy Vědu Průmysl*, **36,** 78–81 (1942); through *Chemisches Zentralblatt*, II, 511–512 (**1942**).

Name: For J. Hanuš, Czech chemist.

Chemical Properties: Formula $H_2Mg_2Si_3O_9 \cdot H_2O$. Analysis gave SiO_2 57.37, MgO 18.55, CaO 4.84, MnO 0.54, FeO 3.57, H_2O (above 200°) 6.49, H_2O (below 200°) 8.68%. A dehydration curve indicates that the water given off below 200° is adsorbed, most of the remainder is given off at 700°. Completely decomposed by HCl with separation of silica, slowly decomposed by H_2SO_4 and $HClO_4$, slightly acted on by HNO_3.

Physical Properties: Occurs as yellowish-white to yellow-brown radiating aggregates similar to pectolite. $H=1\text{–}1\frac{1}{2}$, $G=2.166$. Optically biaxial with large axial angle. Birefringence greater than that of sepiolite. The x-ray powder pattern differs from that of sepiolite.

Occurrence: Occurs as a pseudomorph after apophyllite in the region of Liebstadtl, Riesengebirge.

Relations: The mineral is thought by Kašper to be the magnesium end of the pectolite-walkerite series.

Discussion: This material seems to correspond fairly closely to stevensite, a pseudomorph after pectolite, cf. Glenn, *Am. Mineral.*, **1,** 44 (1916). Further study is needed.

Michael Fleischer

Dr. D. Jerome Fischer of the Department of Geology, University of Chicago, is spending the summer investigating the beryllium and tantalum content of the Pala pegmatites in California. He expects to return to Chicago about October 1.